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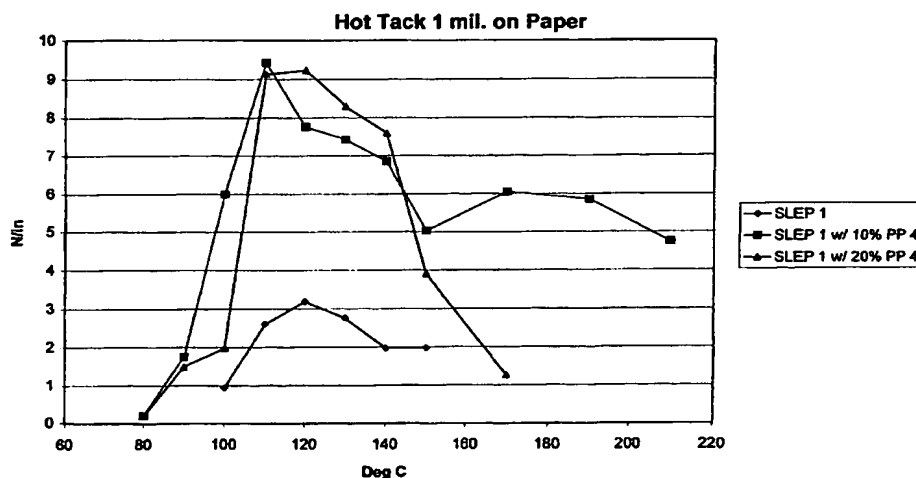
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(54) Title: **POLYMER COMPOSITIONS WHICH EXHIBIT HIGH HOT TACK**



(57) Abstract: The present invention relates to film layers and compositions having improved hot tack properties. The compositions comprise polypropylene and linear ethylene polymer, substantially linear ethylene polymer or low density ethylene polymer. The compositions are suitable for use, for example, laminates or films in packaging applications.



WO 00/78859 A1



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

POLYMER COMPOSITIONS WHICH EXHIBIT HIGH HOT TACK

The present invention relates to polymer compositions having improved hot tack properties and which are often suitable for coatings and films. More particularly, the invention relates to laminates or multi-layer films having at least one film layer
5 comprising polypropylene or a copolymer thereof and linear ethylene polymer, substantially linear ethylene polymer or low density ethylene polymer.

It is often desirable to coat an article, substrate or film in order to modify the properties. A particularly desirable coating is that of a heat-sealable film; that is, a film which is capable of being bonded to itself, another film or another substrate with the
10 application of heat and/or pressure. In this manner, the article, substrate or film can be sealed to form structures such as bags or other packaging materials.

Laminates and single or multi-layer films are packaging materials that often employ heat-sealable layers. Laminates are often made by coating a substrate, for example, paper or film, with a heat-sealable layer by extrusion coating. Extrusion coating
15 is a process whereby a polymer or blend of polymers is fed into an extruder hopper. In the extruder, the polymer or blend is melted and passed at a die to form a web. The web is then extruded onto the substrate through a nip roll/chill roll interface, for example, so that the molten web is pressed onto the substrate. The substrate is cooled by the chill roll and the wound up at a winder.

Similarly, many different processes are often employed to make single or multi-
20 layer films which are useful as packaging materials. Such processes can include bubble extrusion and biaxial orientation processes, as well as, tenter frame techniques. In order to facilitate sealing, the heat-sealable film is usually employed singly or as the outermost or innermost layer in the case of multi-layer films.

Laminates and single or multi-layer films having a heat-sealable film layer are
25 often used in "form, fill, and seal" machines. These machines create from film a continuous stream of packages that are capable of being closed by film-to-film seals. Often such packages are sealed via heat seal jaws that apply heat and pressure to form the film-to-film seal closure.

The heat seal closures made via the heat seal jaws will often be strongest after the
30 seal has cooled to ambient temperature. However, in order to increase the production

capacity, the packages are often filled with product before the bottom seal has had time to completely cool, therefore, the polymers at the seal interface haven't completely solidified (or recrystallized) or they are still in a softened state. Thus, the closure must exhibit a sufficient strength very rapidly without the need for cooling to ambient temperature.

5 Otherwise, the closure will be destroyed by the weight of the product when the package is filled.

"Seal strength" is the strength of a heat seal at ambient temperature after the seal has been formed and reached its full strength. However, as described above, the properties of the seal at temperatures subsequent to formation but prior to cooling to

10 ambient conditions are often important. The properties of seal strength at temperatures above ambient are often referred to as "hot tack" properties.

There are a number of different hot tack properties that are important for heat-sealable films. One important hot tack property is the "initiation temperature." The initiation temperature is the first temperature above ambient at which a seal can be formed

15 by applying a given pressure to a given thickness of film for a given length of time. In general, lower initiation temperatures are desirable because less energy is required to be used to form the seal and also the less time it takes for the initial seal to form at a given seal jaw temperature. Thus, production rates are capable of being increased.

Another important hot tack property is "ultimate hot tack." Ultimate hot tack is

20 the largest strength the seal has at temperatures above the initiation temperature. Usually it is desirable that the ultimate hot tack occurs at the lowest possible temperature. Another hot tack property that is generally desirable is a wide processing window such that the film exhibits a suitable seal strength as measured over a broad temperature range. Also generally desirable is high temperature hot tack such that the seal strength remains

25 sufficient even at elevated temperatures.

The hot tack properties are often determined by the composition employed to form the film seal. In the past, compositions such as those described in U.S.-A-Patent No. 4,339,507 and U.S.-A-Patent No. 5,741,861 that are a mixture of, for example, low density polyethylene and linear low density ethylene hydrocarbon copolymer have been

30 employed. Unfortunately, however, such compositions often have hot tack properties that

may limit the production capacity. Thus, it would be desirable to discover new compositions that have improved hot tack properties.

Advantageously, a new composition has been discovered which gives superior hot tack properties. The composition comprises

5 (a) from 2 to 13 percent by weight of polypropylene which is a homopolymer or a copolymer derived from at least about 80 percent propylene monomer and less than about 20 percent alpha-olefin monomer, based on the total weight of the monomers, and which has a melt flow rate of from 1.0 to 50 dg/minute as measured in accordance with ASTM D-1238, Condition 230° C/2.16kg.

10

(b) from 87 to 98 percent by weight of a polymer selected from the group consisting of linear ethylene polymer, substantially linear ethylene polymer, low density ethylene polymer, and mixtures thereof;

15

wherein the linear ethylene polymer or substantially linear ethylene polymer is characterized by:

- (1) a density of from 0.87 to 0.960 g/cm³,
- (2) a molecular weight distribution, M_w/M_n , of less than or equal to about 5, and
- 20 (3) a melt index, I_2 , as measured in accordance with ASTM D-1238, Condition 190° C/2.16 kg, of from 0.5 to 20.0 dg/minute; and

wherein the low density ethylene polymer is characterized by:

- (1) a density of from 0.91 to 0.96 g/cm³, and
- 25 (2) a melt index, I_2 , as measured in accordance with ASTM D-1238, Condition 190° C/2.16 kg of from 0.1 to 20.0 dg/minute.

The composition is suitable for forming a film having improved hot tack and for use in coating substrates. In this manner, a heat-sealable film may be made for packaging materials. The packaging materials are beneficial in that they exhibit surprising and
30 unexpected hot tack properties and facilitate production.

When used in extrusion coating, the compositions of the instant invention often form homogeneous extrudates, give stable extrusion rates at high take-off speeds, have acceptable neck-in, give good product properties such as hot tack, tensile strength, wide temperature range processability, and good tear and abrasion resistance.

5 Fig. 1 shows the hot tack performance of compositions of the present invention coated on paper as compared to a composition of polyethylene.

Fig. 2 shows the hot tack performance of compositions of the present invention coated on foil as compared to a composition of polyethylene.

10 Fig. 3 shows the hot tack performance of compositions of the present invention coated on oriented polypropylene as compared to a composition of polyethylene.

Fig. 4 shows the hot tack performance of compositions of the present invention coated on poly(ethylene terephthalate) as compared to a composition of polyethylene.

Test Procedures and Definitions

Unless indicated otherwise, the following testing procedures are to be employed:

15 Density is measured in accordance with ASTM D-792. The samples are annealed at ambient conditions for 24 hours before the measurement is taken.

20 Melt index (I_2), (measured in the case of the homogeneous linear ethylene polymer, substantially linear ethylene polymer or low density ethylene polymer) is measured in accordance with ASTM D-1238, condition 190° C/2.16 kg (formerly known as "Condition (E)").

Melt flow rate (measured in the case of the polypropylene polymers) is measured in accordance with ASTM D-1238, condition 230° C/2.16 kg (formerly known as "Condition (L)").

25 Molecular weight is determined using gel permeation chromatography (GPC) on a Waters 150C high temperature chromatographic unit equipped with three mixed porosity columns (Polymer Laboratories 10^3 , 10^4 , 10^5 , and 10^6), operating at a system temperature of 140° C. The solvent is 1,2,4-trichlorobenzene, from which 0.3 percent by weight solutions of the samples are prepared for injection. The flow rate is 1.0 mL/min. and the injection size is 100 microliters.

30 The molecular weight determination is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their

elution volumes. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Word in Journal of Polymer Science, Polymer Letters, Vol. 6, (621) 1968 to derive the following equation:

5
$$M_{\text{polyethylene}} = a * (M_{\text{polystyrene}})^b.$$

In this equation, $a = 0.4316$ and $b = 1.0$. Weight average molecular weight, M_w , is calculated in the usual manner according to the following formula: $M_w = \sum w_i * M_i$, where w_i and M_i are the weight fraction and molecular weight, respectively, of the i th fraction eluting from the GPC column.

10 By "draw resonance" is meant a limit cycle corresponding to a sustained periodic oscillation in the velocity and cross-sectional area of a drawing process when the boundary conditions are a fixed velocity at the exit of an extruder and a fixed velocity at the take-off position.

By "neck-in" is meant the reduction in a film web width as it is extruded from a
15 die and which will be caused by a combination of swelling and surface tension effects as the material leaves the die. Neck-in is measured as the distance between the extrudate web as it emerges from the die minus the width of the extrudate web as it is taken up.

The term "composition" as used herein includes a mixture of the materials which comprise the composition, as well as, products formed by the reaction or the
20 decomposition of the materials which comprise the composition.

The term "derived from" means made or mixed from the specified materials, but not necessarily composed of a simple mixture of those materials. Compositions "derived from" specified materials may be simple mixtures of the original materials, and may also include the reaction products of those materials, or may even be wholly composed of
25 reaction or decomposition products of the original materials.

Polypropylene

The composition of the present invention is suitable for forming films that exhibit surprising and unexpected hot tack. The amount of polypropylene in the composition will vary depending on the hot tack properties desired, the other components, the type of
30 polypropylene, and the substrate. However, the composition generally comprises at least

about 2, preferably at least about 3, more preferably at least about 4 percent by weight of polypropylene. Correspondingly, the amount is typically less than about 13, preferably less than about 12, more preferably less than about 10, most preferably less than about 7 percent by weight polypropylene.

5 The polypropylene is generally in the isotactic form of homopolymer polypropylene, although other forms of polypropylene can also be used (for example, syndiotactic polypropylene). Polypropylene impact copolymers (for example, those wherein a secondary copolymerization step comprised of reacting an alpha-olefin monomer such as a C_2-C_8 alpha-olefin such as ethylene with a propylene monomer so that
10 the amount of alpha-olefin monomer in the impact modified polypropylene product is less than about 20 weight percent) and random copolymers (also usually reactor modified and usually containing 1.5 to 8 weight percent of alpha-olefin such as ethylene copolymerized with the propylene), however, can alternatively be used. A complete discussion of various polypropylene polymers useful herein is contained in Modern Plastics
15 Encyclopedia/89, mid October 1988 Issue, Volume 65, Number 11, pp. 86-92.

 The molecular weight of the polypropylene for use in the present invention is conveniently indicated using a melt flow measurement according to ASTM D-1238, Condition 230° C/2.16 kg (formerly known as "Condition (L)" and also known as I_2). Melt flow rate is inversely proportional to the molecular weight of the polymer. Thus, the
20 higher the molecular weight, the lower the melt flow rate, although the relationship is not linear. The melt flow rate for the polypropylene useful herein is generally at least about 1.0, preferably at least about 6.0 dg/min. Correspondingly, the melt flow rate is generally less than about 50, preferably less than 15 dg/min.

 If clarity of the film is desired in, for example, a packaging film, then the
25 refractive index of the polypropylene polymer should be within 0.005, preferably within 0.002 refractive index units, typically measured at 589 nm, from the linear ethylene polymer, substantially linear ethylene polymer, low density ethylene polymer, or mixture thereof. Generally, polypropylene has a refractive index from 1.470 to 1.515 at 589 nm, for example, clarified polypropylene homopolymer has a refractive index of about 1.5065
30 and clarified polypropylene random copolymer has a refractive index of about 1.5044 at 589 nm.

Refractive index is measured using an Abbe-3L Refractometer made by Milton Roy Company and operated at 589 nm (sodium "d" line). Samples are prepared for testing in the refractometer by injection molding the polymer in a BOY 30T injection molder to a thickness of about 0.125 inches. The samples tested for physical properties are prepared in the same manner and also at a thickness of about 0.125 inches.

Chum, Silvis, and Kao, in the presentation entitled "INSITE Technology Based Polyolefin Elastomers for Impact Modification", SPO '93, presented a plot of refractive index versus density for linear ethylene polymers. From this, they derived the equations:
$$RI = 0.69694 (\text{density}) + 0.87884$$

$$\text{density} = (RI - 0.87884)/0.69694$$

where RI is the refractive index of the polymer. Accordingly, when it is desirable to use a clarified polypropylene random copolymer having a refractive index of about 1.5044, preferred homogeneous linear and substantially linear ethylene polymers will have a density of about 0.898 g/cm³.

To promote clarity, the viscosity of the polypropylene polymer should be less than that of the linear ethylene polymer, substantially linear ethylene polymer, low density ethylene polymer, or mixture thereof. Viscosity is inversely proportional to the melt index (in the case of the ethylene polymers) and to the melt flow rate (in the case of the polypropylene polymer). An estimate for comparing polyethylene melt index to polypropylene melt flow rate is to divide the polypropylene melt flow rate by 3. Thus a polypropylene having a melt flow rate of 12 g/10 min. is somewhat like a polyethylene having a melt index of 4 g/10 min., in terms of its viscosity or flow behavior. Accordingly, using a polypropylene having a melt flow rate of 2 or 4 g/10 min. with an ethylene polymer having a melt index of 1.6 g/10 min. would result in a blend in which the higher viscosity component constitutes the minor component of the blend, and would therefore not be preferred for obtaining low haze and high clarity film structures. In contrast, using a polypropylene having a melt flow rate of 12 g/10 min. with an ethylene polymer having a melt index of 1.6 g/10 min. would result in a blend in which the lower viscosity component constitutes the lower viscosity component of the blend, leading to improved dispersion of the minor component in the dominant homogeneous linear or

substantially linear ethylene polymer phase, and thus providing excellent optical properties.

Linear and Substantially Linear Ethylene Polymers

By way of definition, as used herein, "interpolymer" means a polymer of two or
5 more comonomers, *for example* a copolymer, terpolymer, *etc.*

Interpolymers which are useful in the present invention are linear ethylene polymers and substantially linear ethylene polymers. The amount of such polymers, if any, in the composition will vary depending on the hot tack properties desired, the other components, the type of linear or substantially linear polyethylene, and the substrate, if
10 present.

The linear or substantially linear ethylene polymers which may be employed herein are characterized by a density of at least about 0.87, preferably at least 0.89 g/cm³. Correspondingly, the density is usually less than 0.96, preferably less than about 0.94 g/cm³.

15 Another characteristic of the linear or substantially linear ethylene polymers which may be employed herein is a molecular weight distribution, M_w/M_n of less than or equal to about 5, preferably less than or equal to about 4.

Yet another characteristic of the linear or substantially linear ethylene polymer which may be employed herein is a melt index, I_2 , as measured in accordance with ASTM
20 D-1238, Condition 190° C/2.16 kg of from 0.5 to 20.0 dg/min. It has been discovered that linear ethylene polymers or substantially linear ethylene polymers having the aforementioned properties yield compositions in accordance with the present invention which have a high hot tack.

The linear or substantially linear ethylene polymer which may be employed herein
25 may be a homopolymer or copolymer of ethylene with one or more monomers. Preferred monomers or copolymers of ethylene with one or more monomers. Preferred monomers include C₃-C₈ alpha-olefins such as 1-butene, 1-pentene, 4-methyl-1-pentene 1-hexene, 1-heptene, and 1-octene.

The linear ethylene polymer may be an ethylene polymer prepared using a
30 transition metal catalyst, for example, a single site catalyst or a Ziegler-Natta catalyst.

The term "linear ethylene polymer" comprises both homogeneous linear ethylene polymers and heterogeneous linear ethylene polymers. By the term "homogenous", it is meant that any comonomer is randomly distributed within a given interpolymer molecule and substantially all of the interpolymer molecules have the same ethylene/comonomer ratio within that interpolymer. However, unlike heterogeneous polymers, when a homogeneous polymer has a melting peak greater than 115° C (such as is the case of polymers having a density greater than 0.940 g/cm³), such polymers do not additionally have a distinct lower temperature melting peak.

Further, most homogeneous linear ethylene polymer and all substantially linear ethylene polymers will lack a measurable high density fraction, (that is, an essentially linear or homopolymer fraction as measured by Temperature Rising Elution Fractionation which is described in U.S.-A-Patent No. 5,089,321, and which is incorporated in its entirety into and made a part of this application), for example they will not contain any polymer fraction that has a degree of branching less than or equal to 2 methyl/1000 carbons.

The homogeneous linear ethylene polymers or substantially linear ethylene polymers are characterized as having a narrow molecular weight distribution (M_w/M_n). For the homogenous linear ethylene polymer and substantially linear ethylene polymers, the M_w/M_n is from 1.5 to 3.0, preferably from 1.8 to 2.2.

The distribution of comonomer branches for the homogeneous linear ethylene polymer and substantially linear ethylene polymers is characterized by its SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index) and is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The CDBI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described, for example, by Wild *et al.*, Journal of Polymer Science, Poly. Phys. Ed., Vol. 20, p. 441 (1982), or in U.S.-A-Patent Nos. 4,798,081 and 5,008,204. The SCBDI or CDBI for the homogeneous linear ethylene polymer and substantially linear ethylene polymers useful in the compositions of the present invention is preferably greater than

about 50 percent, especially greater than about 70 percent, more preferably greater than about 90 percent.

Homogeneous linear ethylene/ α -olefin interpolymers may be prepared using polymerization processes (for example, as described by Elston in U.S.-A-Patent No. 3,645,992) which provide a homogeneous short chain branching distribution. In his polymerization process, Elston uses soluble vanadium catalyst systems to make such polymers. However, others such as Mitsui Petrochemical Company and Exxon Chemical Company have used so-called single site catalyst systems to make polymers having a homogeneous linear structure. Homogeneous linear ethylene/ α -olefin interpolymers are currently commercially available from Mitsui Petrochemical Company under the tradename "Tafmer" and from Exxon Chemical Company under the tradenames "Exact" and "Exceed".

In contrast to homogeneous linear ethylene polymers (which have fewer than 0.01 long chain branches per 1000 carbons), substantially linear ethylene polymers are homogeneous polymers having long chain branching. In particular, as used herein, "substantially linear" means that the polymer backbone is substituted with about 0.01 long-chain branches/1000 carbons to about 3 long-chain branches/1000 carbons, preferably from 0.01 long-chain branches/1000 carbons to 1 long-chain branch/1000 carbons, and more preferably from 0.05 long-chain branches/1000 carbons to 1 long-chain branch/1000 carbons.

Long chain branching (LCB) is defined herein as a chain length of at least one (1) carbon less than the number of carbons in the comonomer, whereas short chain branching (SCB) is defined herein as a chain length of the same number of carbons in the residue of the comonomer after it is incorporated into the polymer molecule backbone. For example, a substantially linear ethylene/1-octene polymer has backbones with long chain branches of at least seven (7) carbons in length, but it also has short chain branches of only six (6) carbons in length.

Long chain branching can be distinguished from short chain branching by using ^{13}C nuclear magnetic resonance (NMR) spectroscopy and to a limited extent, for example, for ethylene homopolymer it can be quantified using the method of Randall (Rev. Macromol. Chem. Phys., C29 (2&3), p. 285-297. However, as a practical matter, current ^{13}C nuclear magnetic resonance spectroscopy cannot determine the length of a long chain

branch in excess of about six (6) carbon atoms and as such, this analytical technique cannot distinguish between a seven (7) carbon branch and a seventy (70) carbon branch. The long chain branch can be as long as about the same length as the length of the polymer backbone.

5 The homogeneous linear ethylene polymers and substantially linear ethylene polymers used in the composition of this invention are known. The substantially linear ethylene polymers and their method of preparation are fully described in, for example, U.S.-A-Patent Nos. 5,272,236 and 5,278,272, both of which are incorporated in their entirety into and made a part of this application.

10 Methods for determining the amount of long chain branching present, both qualitatively and quantitatively, are known in the art. For qualitative methods for determination, see, for example, U.S.-A-Patent Nos. 5,272,236 and 5,278,272, which disclose the use of an apparent shear stress vs. apparent shear rate plot to identify melt fracture phenomena.

15 For quantitative methods for determining the presence of long chain branching, see, for example, U.S.-A-Patent Nos. 5,272,236 and 5,278,272; Randall (Rev. Macromol. Chem. Phys., C29 (2&3), p. 285-297), which discusses the measurement of long chain branching using ¹³C nuclear magnetic resonance spectroscopy, Zimm, G.H. and Stockmayer, W.H., J. Chem. Phys., 17, 1301 (1949); and Rudin, A., Modern Methods of
20 Polymer Characterization, John Wiley & Sons, New York (1991) pp. 103-112, which discusses the use of gel permeation chromatography coupled with a low angle laser light scattering detector (GPC-LALLS) and gel permeation chromatography coupled with a differential viscometer detector (GPC-DV).

 The "rheological processing index" (PI) is the apparent viscosity (in kpoise) of a
25 polymer measured by a gas extrusion rheometer (GER). The gas extrusion rheometer is described by M. Shida, R.N. Shroff and L.V. Cancio in Polymer Engineering Science, Vol. 17, No. 11, p. 770 (1977), and in Rheometers for Molten Plastics by John Dealy, published by Van Nostrand Reinhold Co. (1982) on pp. 97-99. GER experiments are performed at a temperature of 190°C, at nitrogen pressures between 250 to 5500 psig
30 using about a 0.754 millimeter diameter, 20:1 L/D die with an entrance angle of 180°. For the substantially linear ethylene polymers useful herein, the PI is the apparent

viscosity (in kpoise) of a material measured by GER at an apparent shear stress of 2.15×10^6 dyne/cm² (0.215 MPa). The substantially linear ethylene polymers useful herein preferably have a PI in the range of 0.01 kpoise to 50 kpoise, preferably about 15 kpoise or less. The substantially linear ethylene polymers useful herein have a PI less than or equal to about 70 percent of the PI of a comparative linear ethylene polymer (either a Ziegler polymerized polymer or a linear uniformly branched polymer as described by Elston in U.S.-A-Patent No. 3,645,992) at about the same I_2 and M_w/M_n .

Substantially linear ethylene polymers will further be characterized as having a resistance to melt fracture. An apparent shear stress versus apparent shear rate plot is used to identify the melt fracture phenomena. According to Ramamurthy in the Journal of Rheology, 30(2), 337-357, 1986, above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

Surface melt fracture occurs under apparently steady flow conditions and ranges in detail from loss of specular film gloss to the more severe form of "sharkskin." The onset of surface melt fracture (OSMF) is characterized at the beginning of losing extrudate gloss at which the surface roughness of the extrudate can only be detected by 40x magnification. The critical shear rate at the onset of surface melt fracture for the substantially linear ethylene interpolymers and homopolymers is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a comparative linear ethylene polymer (either a Ziegler polymerized polymer or a linear uniformly branched polymer as described by Elston in USA Patent No. 3,645,992) having about the same I_2 and M_w/M_n .

Gross melt fracture occurs at unsteady extrusion flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability, (for example, in blown films and bags therefrom), surface defects should be minimal, if not absent, for good film quality and properties. The critical shear stress at the onset of gross melt fracture for the substantially linear ethylene polymers used in making the film structures of the present invention is greater than about 4×10^6 dynes/cm² (0.4 MPa). The critical shear rate at the onset of surface melt fracture

(OSMF) and the onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER.

The substantially linear ethylene polymers will be characterized as having an I_{10}/I_2 (ASTM D-1238), which is greater than or equal to 5.63, and is preferably from 6.5 to 15, more preferably from 7 to 10. The molecular weight distribution (M_w/M_n), measured by gel permeation chromatography (GPC), is defined by the equation:
 $M_w/M_n \leq (I_{10}/I_2) - 4.63$, and is preferably between 1.5 and 2.5. For the substantially linear ethylene polymers, the I_{10}/I_2 ratio indicates the degree of long-chain branching, *that is* the larger the I_{10}/I_2 ratio, the more long-chain branching in the polymer.

Substantially linear ethylene polymers have a highly unexpected flow property, where the I_{10}/I_2 value of the polymer is essentially independent of the polydispersity index (*that is*, M_w/M_n) of the polymer. This is contrasted with conventional linear homogeneously branched and linear heterogeneously branched polyethylene resins having rheological properties such that to increase the I_{10}/I_2 value the polydispersity index must also be increased.

The homogeneous linear ethylene polymer or substantially linear ethylene polymer may be suitably prepared using a constrained geometry metal complex, such as are disclosed in U.S. Application Serial No. 545,403, filed July 3, 1990 (EP-A-416,815); U.S. Application Serial No. 702,475, filed May 20, 1991 (EP-A-514,828); as well as U.S.-A-5,470,993, 5,374,696, 5,231,106, 5,055,438, 5,057,475, 5,096,867, 5,064,802, and 5,132,380. In U.S. Application Serial No. 720,041, filed June 24, 1991, (EP-A-514,828) certain borane derivatives of the foregoing constrained geometry catalysts are disclosed and a method for their preparation taught and claimed. In U.S.-A-5,453,410 combinations of cationic constrained geometry catalysts with an alumoxane were disclosed as suitable olefin polymerization catalysts.

The heterogeneous linear ethylene polymers are homopolymers of ethylene or copolymers of ethylene and one or more C_3 to C_8 alpha olefins. Both the molecular weight distribution and the short chain branching distribution, arising from alpha olefin copolymerization, are relatively broad compared to homogeneous linear ethylene polymers. Heterogeneous linear ethylene polymers can be made in a solution, slurry, or

gas phase process using a Ziegler-Natta catalyst, and are well known to those skilled in the art. For example, see U.S.-A-Patent No. 4,339,507.

Low Density Ethylene Polymer

The amount, if any, of low density ethylene polymer, that is, low density polyethylene, in the composition will vary depending on the hot tack properties desired, the other components, the type of low density polyethylene, and the substrate, if present.

The low density ethylene polymer may be a homopolymer of ethylene or a copolymer of ethylene and another monomer that is produced, for example, by a free radical polymerization. Suitable low density ethylene polymers are described in, for example, GB 1,096,945 and U.S.-A-Patent No. 2,825,721. The other monomers are often copolymerized with ethylene to produce a polymer having different properties than that of the homopolymer. If employed, comonomer is generally incorporated at 1 to 20 weight percent based on the weight of the monomers. Preferred comonomers include acetates (such as vinyl acetate), acrylics (such as acrylic or methacrylic acid), and acrylates (such as methylacrylate, butylacrylate, methylmethacrylate, or hydroxyethylmethacrylate). The melt index of the low density ethylene polymer useful herein is typically from 0.1 to 20, preferably from 0.4 to 12 dg/min. Generally, increasing the average molecular weight within this range, that is, lowering the melt index, usually produces a composition which is useful for making a film having increased tensile strength, increased impact properties, increased seal strength, and lower optical properties.

The density of the low density ethylene polymers which are useful herein varies depending on whether homopolymer or copolymers are to be employed but is usually from 0.91-0.96 g/cm³. The density of the homopolymer low density ethylene polymer is generally from 0.91 to 0.94, preferably from 0.915 to 0.925 g/cm³. The density of copolymer low density ethylene polymer is generally from 0.92 to 0.96 g/cm³, preferably from 0.93 to 0.95 g/cm³.

Preferred Compositions

The preferred compositions of the instant invention typically comprise at least about 87, preferably at least about 90 weight percent of linear ethylene polymer, substantially linear ethylene polymer, low density ethylene polymer or a mixture thereof.

Correspondingly, the preferred compositions typically comprise no more than about 98, preferably no more than about 96 weight percent of linear ethylene polymer, substantially linear ethylene polymer, low density ethylene polymer or a mixture thereof.

Typically, the compositions of the present invention increase the ultimate hot tack
5 by at least 15 percent, preferably at least 25 percent over similar compositions which do not have polypropylene. Also, the compositions of the present invention often exhibit initiation temperatures which are at least 5, preferably at least 10° C lower than similar compositions which do not have polypropylene.

Preferred compositions of the present invention for extrusion coating often include
10 mixtures of the linear ethylene polymer or substantially linear ethylene polymer and low density ethylene polymer. The amount of each polymer within the composition will vary depending upon the desired characteristics and the amount and type of polypropylene.

A particularly preferable composition of the present invention for extrusion coating comprises from 2 to 13 weight percent polypropylene, from 67 to 93, more
15 preferably from 80 to 90, weight percent linear ethylene polymer or substantially linear ethylene polymer and from 5 to 20 weight percent low density polyethylene

The preferred compositions for extrusion coating of the present invention often exhibit a melt index, I_2 as measured in accordance with ASTM D-1238, Condition 190° C/2.16 kg of from 4 to 20 dg/min. and a density of from 0.89 to 0.91 g/cm³.
20 Compositions of this type often exhibit advantageous low neck-in and/or low or no draw resonance inr extrusion coating applications.

Heat Sealable Films Made with the Composition of the Present Invention

The compositions of the present invention may be formed in any convenient manner. Typically, it is suitable to melt blend the individual components. In the case of
25 melt blending, the polymers are first mixed and then extruded in a compounding extruder in order to obtain pellets that contain a combination of the materials. Typically, the pellets are from 10 to 120 pellets / gram, preferably from 20 to 40 pellets / gram.

If forming a heat sealable film having the inventive composition, then it is also suitable to dry blend the individual components. In dry blending, pellets of the different materials are mixed together and then added directly to the extruder used to manufacture the film. Optionally, additional additives such as slip, anti-block, and polymer process aid can be incorporated in either the melt blends or dry blends.

Heat sealable films made with the composition of the present invention may be employed in either monolayer or multilayer film structures or as laminates. Regardless of how the film is utilized, it may be prepared by a variety of processes that are well known to those of skill in the art.

Film structures may be made by conventional fabrication techniques, for example simple bubble extrusion, biaxial orientation processes (such as tenter frames, trapped bubble, or double bubble processes), simple cast/sheet extrusion, coextrusion, lamination, *etc.* Conventional simple bubble extrusion processes (also known as hot blown film processes) are described, for example, in The Encyclopedia of Chemical Technology, Kirk-Othmer, Third Edition, John Wiley & Sons, New York, 1981, Vol. 16, pp. 416-417 and Vol. 18, pp. 191-192. Biaxial orientation film manufacturing processes such as described in the "double bubble" process of U.S.-A-Patent No. 3,456,044 (Pahlke), and the processes described in U.S.-A-Patent No. 4,352,849 (Mueller), U.S.-A-Patent Nos. 4,820,557 and 4,837,084 (both to Warren), U.S.-A-Patent No. 4,865,902 (Golike et al.), U.S.-A-Patent No. 4,927,708 (Herran et al.), U.S.-A-Patent No. 4,952,451 (Mueller), and U.S.-A-Patent Nos. 4,963,419 and 5,059,481 (both to Lustig et al.), can also be used to make the novel film structures of this invention. Biaxially oriented film structures can also be made by a tenter-frame technique, such as that used for oriented polypropylene.

Other multilayer film manufacturing techniques for food packaging applications are described in Packaging Foods With Plastics by Wilmer A. Jenkins and James P. Harrington (1991), pp. 19-27, and in "Coextrusion Basics" by Thomas I. Butler, Film Extrusion Manual: Process, Materials, Properties, pp. 31-80 (published by TAPPI Press (1992)).

In certain embodiments of this invention, at least one heat sealable, innermost or outermost layer (that is, skin layer) of a film structure comprises the blend of the polypropylene polymer and linear or substantially linear ethylene polymer, low density

polyethylene or mixture. This heat sealable layer can be coextruded with other layer(s) or the heat sealable layer can be laminated onto another layer(s) or substrate in a secondary operation, such as that described in Packaging Foods With Plastics, *ibid*, or that described in "Coextrusion For Barrier Packaging" by W. J. Schrenk and C. R. Finch, Society of
5 Plastics Engineers RETEC Proceedings, June 15-17 (1981), pp. 211-229. Preferable substrates include papers, foils, oriented polypropylenes such as industrial grade or BICOR LBW®, polyamides, polyesters, polyethylenes, polyethylene terephthalate, and, metallized substrates.

Should a multilayer film be desired, such may be obtained from a monolayer film
10 which has been previously produced via tubular film (that is, blown film techniques) or flat die (that is, cast film) as described by K. R. Osborn and W. A. Jenkins in Plastic Films, Technology and Packaging Applications (Technomic Publishing Co., Inc. (1992), wherein the sealant film must go through an additional post-extrusion step of adhesive or extrusion lamination to other packaging material layers. If the sealant film is a
15 coextrusion of two or more layers (also described by Osborn and Jenkins), the film may still be laminated to additional layers of packaging materials, depending on the other physical requirements of the final packaging film. "Laminations vs. Coextrusions" by D. Dumbleton (Converting Magazine, September 1992) also discusses lamination versus coextrusion. Monolayer and coextruded films can also go through other post-extrusion
20 techniques, such as a biaxial orientation process and irradiation. With respect to irradiation, this technique can also precede extrusion by irradiating the pellets from which the film is to be fabricated prior to feeding the pellets into the extruder, which increases the melt tension of the extruded polymer film and enhances processability.

Extrusion coating is yet another technique for producing packaging materials.
25 Similar to cast film, extrusion coating is a flat die technique. A heat-sealable film comprised of the compositions of the present invention can be extrusion coated onto a substrate either in the form of a monolayer or a coextruded extrudate according to, for example, the processes described in U.S.-A-Patent No. 4,339,507. Utilizing multiple extruders or by passing the various substrates through the extrusion coating system
30 several times can result in multiple polymer layers each providing some sort of performance attribute whether it be barrier, toughness, or improved hot tack or heat sealability. Some typical end use applications for multi-layered/multi-substrate systems

are for cheese packages. Other end use applications include, but are not limited to, moist pet foods, snacks, chips, frozen foods, meats, hot dogs, and numerous other applications.

In those embodiments in which the film comprises the blend of the homogeneous linear ethylene polymer or substantially linear ethylene polymer and/or low density ethylene polymer, and the polypropylene polymer, other layers of the multilayer structure may be included to provide a variety of performance attributes. These layers can be constructed from various materials, including blends of homogeneous linear or substantially linear ethylene polymers with polypropylene polymers, and some layers can be constructed of the same materials, for example some films can have the structure A/B/C/B/A wherein each different letter represents a different composition. Representative, nonlimiting examples of materials in other layers are: poly(ethylene terephthalate) (PET), ethylene/vinyl acetate (EVA) copolymers, ethylene/acrylic acid (EAA) copolymers, ethylene/methacrylic acid (EMAA) copolymers, LLDPE, HDPE, LDPE, graft-modified ethylene polymers (for example maleic anhydride grafted polyethylene), styrene-butadiene polymers (such as K-resins, available from Phillips Petroleum), etc. Generally, multilayer film structures comprise from 2 to 7 layers.

The thickness of the multilayer structures is typically from 1 mil to 4 mils (25 to 102 micrometers) (total thickness). The heat sealable film layer varies in thickness depending on whether it is produced via coextrusion or lamination of a monolayer or coextruded film to other packaging materials. In a coextrusion, the heat sealable film layer is typically from 0.1 to 3 mils (2.5 to 75 μm), preferably from 0.4 to 2 mils (10 to 51 μm). In a laminated structure, the monolayer or coextruded heat sealable film layer is typically from 0.5 to 2 mils (13 to 51 μm), preferably from 1 to 2 mils (25 to 51 μm). For a monolayer film, the thickness is typically between 0.4 mil to 4 mils (10 to 102 μm), preferably between 0.8 to 2.5 mils (20 to 64 μm).

The heat sealable films of the invention can be made into packaging structures such as form-fill-seal structures or bag-in-box structures. For example, one such form-fill-seal operation is described in Packaging Foods With Plastics, ibid, pp. 78-83. Packages can also be formed from multilayer packaging roll stock by vertical or horizontal form-fill-seal packaging and thermoform-fill-seal packaging, as described in "Packaging Machinery Operations: No. 8, Form-Fill-Sealing, A Self-Instructional

Course" by C. G. Davis, Packaging Machinery Manufacturers Institute (April 1982); The Wiley Encyclopedia of Packaging Technology by M. Bakker (Editor), John Wiley & Sons (1986), pp. 334, 364-369; and Packaging: An Introduction by S. Sacharow and A. L. Brody, Harcourt Brace Javanovich Publications, Inc. (1987), pp.322-326. A particularly
5 useful device for form-fill-seal operations is the Hayssen Ultima Super CMB Vertical Form-Fill-Seal Machine. Other manufacturers of pouch thermoforming and evacuating equipment include Cryovac and Koch. A process for making a pouch with a vertical form-fill-seal machine is described generally in U.S.-A-Patent Nos. 4,503,102 and 4,521,437. Film structures containing one or more layers comprising a heat sealable film
10 of the present invention are well suited for the packaging of potable water, wine, cheese, potatoes, condiments, and similar food products in such form-fill-seal structures.

The compositions and heat sealable films of this invention and their use are more fully described by the following examples. Unless indicated to the contrary, all parts and percentages are by weight.

15 **Examples**

The polymers of the table entitled "Polymers" were utilized in preparing the compositions and films of the examples and comparative examples.

POLYMERS

Polymer Type	Polymer designation	Density (g/cm ³)	I ₂ (g/10 min.)	Mw/Mn	Melting point (Deg C)
Polyolefin Plastomer	SLEP 1	0.902	7.5	2.7	101
Polyolefin Plastomer	SLEP 2	0.898	20		96
AFFINITY* PL1280	SLEP 3	0.900	6	2.50	98
AFFINITY SM8250	SLEP 4	0.885	30		92
LLDPE	LEP 1	0.921	5.4	3.99	119
Exxon's Exact 3139	Ethylene-1-hexene Copolymer	0.902	7.0	2.2	99
INSPIRE* H700-12	PP 1 - Homopolymer	0.90	12 Melt Flow		165
INSPIRE* H500-35	PP 2 - Homopolymer	0.90	35 Melt Flow		165
INSPIRE* C105-2†	PP 3 - Copolymer with 16-20 percent ethylene	0.90	2 Melt Flow		160
Profax® SR549-M	PP 4 - Copolymer with 3-4 percent ethylene	0.90	11.5 Melt Flow		150
DOW LDPE	LDPE 1	0.918	0.47	7.6	105
DOW LDPE	LDPE 2	0.923	4.2	5.78	112
DOW LDPE	LDPE 3	0.918	8.0	6.97	105
DOW LDPE	LDPE 4	0.918	12.0	6.02	105
PRIMACOR* 4608	EAA 1	(6.5 percent AA)	7.7	5.19	99

*A Trademark of The Dow Chemical Company.

Notes: SLEP – substantially linear ethylene polymer

SLEP 1 contains 8 weight percent LDPE

LEP 1 contains 18 weight percent LDPE

PP indicates polypropylene

5 Ethylene-1-hexene copolymer is an Exxon Exact® Plastomer

Profax® is a registered trademark of Montel

† INSPIRE polypropylene is an impact polypropylene copolymer

LDPE indicates low density polyethylene

Melt Flow for Polypropylene is in grams/10 min at 230 Deg C.

10 EAA is a copolymer of ethylene and acrylic acid

AA is the weight percent of acrylic acid in the EAA copolymer

Example 1 – Preparation of Compositions

15 Polymer blends can be prepared in several fashions. Dry blending of each polymer can be achieved by adding the specific amount of each component by weight and then blending by hand or by mechanical means such as tumble or pneumatic blending. Melt blends can also be produced by extrusion compounding resulting in pellets containing each component at their proper concentrations. Each individual polymer could
20 also be introduced into the feed section of the extruder being used to form the final film, laminate, or extrusion coating. Some blend systems were dry blending only, two and three component melt blends, or two component melt blends which were then dry blended with a third component. The blending mechanism didn't negatively effect the boost in performance as claimed by this application.

25 Example 2 – Formation of Laminates

Typically, laminates are formed by extrusion coating of the claimed polymer system onto different substrates at various thicknesses. The resulting structure is then utilized for performance testing. Coextrusion of the polymer system can also be utilized
30 where as the improved hot tack system is at the sealing surface of the resulting multi-layered extrusion. Lamination of films produced by claimed invention onto a variety of substrates will also result in improved hot tack performance when incorporating claimed polymer system. Extrusion coating performance was evaluated on a 3 1/2" (88.9 mm),

30:1 L/D, Black Clawson extrusion coater fitted with a 30" (762 mm) Cloeren internally deckled die and Cloeren feedblock. The die gap was set at 25 mils (625 μm) utilizing a 6 inch (15.2 cm) air gap (the distance from the die opening to the substrate/chill roll interface). The screw speed was maintained at approximately 90 rpm to produce a 1 mil (25 μm) coating while running the various substrates at 440 fpm (13.4 mpm) through the extrusion coater. All paper structures were produced on 50 lb (23 kg) Kraft paper. Other substrates evaluated were produced by slip sheets (attach tape to the leading edge of the substrate to be tested and then dropped onto the traveling Kraft paper thus pulling the sample substrate under the extrusion die onto the chill roll while being coated with the polymer system to be evaluated).

Example 3 – Measurement of Properties of Laminates

Hot tack strengths were evaluated using either a DTC Hot Tack Tester Model No. DTC 52D available from Topwave or a Hot Tack Tester Model 3000 version 2 available from J&B Instruments and the instructions for each therewith. The coated samples (1 inch strips) were sealed at 40 psig bar pressure, with a 0.5 second dwell time, a 0.4 second delay time and a peel speed of 150 mm/sec. Five evaluations were performed on each sample at each temperature and the average value is reported in the tables below. All hot tack data is reported in strength measurements of Newtons/inch (N/in).

TABLE 1

HOT TACK DATA FOR 1 MIL (25 μ m) COATING ONTO PAPER, in Newtons/in. (Newtons/cm.)

Temp (Deg C)	80	80	90	90	100	100	110	110	120	120	130	130	140	140
	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/in	N/cm
Comparative - LEP 1	NM	NM	NM	NM	0.933	0.37	2.594	1.02	3.187	1.25	2.755	1.08	1.968	0.77
SLEP 1 w/ 10 percent PP 4	0.2	0.08	1.753	0.69	5.995	2.36	9.428	3.71	7.756	3.05	7.427	2.92	6.855	2.70
SLEP 1 w/ 20 percent PP 4	0.2	0.08	1.492	0.59	1.977	0.78	9.135	3.60	9.233	3.64	8.298	3.27	7.599	2.99

NM denotes not measurable.

TABLE 1, continued

HOT TACK DATA FOR 1 MIL (25 μ m) COATING ONTO PAPER, in Newtons/in. (Newtons/cm.)

Temp (Deg C)	150	150	170	170	190	190	210	210
	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/in	N/cm
Comparative - LEP 1	1.974	0.78	NM	NM	NM	NM	NM	NM
SLEP 1 w/ 10 percent PP 4	5.026	1.98	6.046	2.38	5.858	2.31	4.745	1.87
SLEP 1 w/ 20 percent PP 4	3.902	1.54	1.259	0.50	NM	NM	NM	NM

NM denotes not measurable.

TABLE 2

HOT TACK DATA FOR 1 MIL (25 μ m) COATING ONTO ALUMINUM FOIL, in Newtons/in. (Newtons/cm.)

Temp (Deg C)	80	80	90	90	100	100	110	110	120	120	130	130	140	140	150	150
	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/in	N/cm
Comparative - SLEP 1	NM		0.253	0.10	2.92	1.15	4.869	1.92	4.808	1.89	4.468	1.76	4.956	1.95	4.24	1.67
SLEP 1 w/ 10 percent PP 4	0.229	0.09	2.24	0.88	5.669	2.23	8.645	3.40	10.375	4.08	10.892	4.29	7.424	2.92	6.73	2.65
SLEP 1 w/ 20 percent PP 4	NM		0.576	0.23	1.994	0.79	4.152	1.63	4.89	1.93	5.334	2.10	9.288	3.66	8.109	3.19

NM denotes not measurable.

TABLE 3

HOT TACK DATA FOR 1 MIL (25 μ m) COATING ONTO BICOR® IG ORIENTED POLYPROPYLENE FROM MOBIL, in Newtons/in. (Newtons/cm.)

Temp (Deg C)	80	80	90	90	100	100	110	110N/cm	120	120	130	130	140	140	150	150
	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/in	cm	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/in	N/cm
Comparative - SLEP 1	0.617	0.24	0.997	0.39	1.282	0.50	1.398	0.55	1.047	0.41	0.972	0.38	0.8	0.31	0.746	0.29
SLEP 1 w/ 10 percent PP 4	0.672	0.26	5.49	2.16	5.74	2.26	4.453	1.75	4.659	1.83	1.937	0.76	0.9	0.35	0.898	0.35
SLEP 1 w/ 20 percent PP 4	0.481	0.19	3.918	1.54	5.626	2.21	4.832	1.90	3.18	1.25	0.568	0.22	0.532	0.21	0.479	0.19

TABLE 4
HOT TACK DATA FOR 1 MIL (25 μ m) COATING ONTO BICOR® LBW OPP
(ORIENTED POLYPROPYLENE FROM MOBIL),
in Newtons/in. (Newtons/cm.)

Temp (Deg C)	80	80	90	90	100	100	110	110N/cm	120	120	130	130	140	140	150	150
	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/in	cm	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/in	N/cm
Comparative	0.39	0.15	1.3	0.51	1.43	0.56	1.24	0.49	1.04	0.41	0.78	0.31	0.94	0.37	1.06	0.42
- SLEP 1																
SLEP 1 w/ 10 percent PP 4	0.68	0.27	4.83	1.90	5.8	2.28	3.94	1.55	3.32	1.31	2.63	1.04	0.82	0.32	1.25	0.49
SLEP 1 w/ 20 percent PP 4	0.484	0.19	2.987	1.18	5.907	2.33	4.682	1.84	2.922	1.15	0.918	0.36	0.801	0.32	NM	NM

NM denotes not measurable.

TABLE 5

HOT TACK DATA FOR 1 MIL (25 μ m) COATING ONTO HOSTAPHAN® 2DEF PRIMED PET
(POLYETHYLENE TEREPHTHALATE) FILM FROM HOECHST DIAFOIL.,
in Newtons/in. (Newtons/cm.)

Temp (Deg C)	80 N/in	80 N/cm	90 N/in	90 N/cm	100 N/in	100 N/cm	110 N/in	110N/ cm	120 N/in	120 N/cm	130 N/in	130 N/cm	140 N/in	140 N/cm	150 N/in	150 N/cm
Comparative - SLEP 1	0.39	0.15	1.3	0.51	1.43	0.56	1.24	0.49	1.04	0.41	0.78	0.31	0.94	0.37	1.06	0.42
SLEP 1 w/ 10 percent PP 4	0.68	0.27	4.83	1.90	5.8	2.28	3.94	1.55	3.32	1.31	2.63	1.04	0.82	0.32	1.25	0.49
SLEP 1 w/ 20 percent PP 4	0.484	0.19	2.987	1.18	5.907	2.33	4.682	1.84	2.922	1.15	0.918	0.36	0.801	0.32	NM	NM

NM denotes not measurable.

TABLE 6
HOT TACK DATA FOR 1 MIL (25 μ m) COATING ONTO PAPER-HIGHER LOADING AND DIFFERENT POLYPROPYLENE,
in Newtons/in. (Newtons/cm.)

Temp (Deg C)	80	80	90	90	100	100	110	110N/cm	120	120	130	130	140	140
	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/in	cm	N/in	N/cm	N/in	N/cm	N/in	N/cm
Comparative	NM	NM	NM	NM	0.534	0.21	3.559	1.40	3.438	1.35	3.472	1.37	2.001	0.79
- SLEP 1														
SLEP 1 w/ 5	NM	NM	0.319	0.13	2.816	1.11	8.035	3.16	8.264	3.25	6.604	2.60	5.158	2.03
percent PP 4														
SLEP 1 w/	NM	NM	0.673	0.26	6.991	2.75	9.863	3.88	9.243	3.64	7.936	3.12	7.49	2.95
10 percent														
PP 4														
SLEP 1 w/	NM	NM	0.539	0.21	2.545	1.00	9.452	3.72	8.195	3.23	8.047	3.17	5.762	2.27
15 percent														
PP 4														
SLEP 1 w/	NM	NM	0.485	0.19	1.999	0.79	8.074	3.18	8.789	3.46	7.23	2.85	6.806	2.68
20 percent														
PP 4														
SLEP 1 w/	NM	NM	1.118	0.44	4.853	1.91	9.599	3.78	8.501	3.35	7.194	2.83	5.944	2.34
25 percent														
PP 4														
SLEP 1 w/ 5	NM	NM	0.73	0.29	4.648	1.83	9.768	3.85	8.02	3.16	6.095	2.40	5.423	2.14
percent PP 1														
SLEP 1 w/	0.262	0.10	1.386	0.55	3.916	1.54	9.894	3.90	10.204	4.02	7.84	3.09	6.741	2.65
10 percent														
PP 1														

NM denotes not measurable.

TABLE 6, continued

HOT TACK DATA FOR 1 MIL (25 μ m) COATING ONTO PAPER-HIGHER LOADING AND DIFFERENT POLYPROPYLENE,
in Newtons/in. (Newtons/cm.)

Temp (Deg C)	150 N/in	150 N/cm	170 N/in	170 N/cm	190 N/in	190 N/cm	210 N/in	210 N/cm
Comparative	1.847	0.73	NM	NM	NM	NM	NM	NM
- SLEP 1								
SLEP 1 w/ 5 percent PP 4	4.007	1.58	3.41	1.34	5.872	2.31	3.048	1.20
SLEP 1 w/ 10 percent PP 4	5.577	2.20	2.215	0.87	NM	NM	NM	NM
SLEP 1 w/ 15 percent PP 4	3.33	1.31	1.682	0.66	NM	NM	NM	NM
SLEP 1 w/ 20 percent PP 4	3.479	1.37	0.667	0.26	NM	NM	NM	NM
SLEP 1 w/ 25 percent PP 4	6.36	2.50	7.607	2.99	4.781	1.88	3.039	1.20
SLEP 1 w/ 5 percent PP 1	5.035	1.98	5.511	2.17	4.545	1.79	5.374	2.12
SLEP 1 w/ 10 percent PP 1	6.195	2.44	6.697	2.64	6.304	2.48	5.195	2.05

NM denotes not measurable.

TABLE 7

HOT TACK DATA FOR 1 MIL (25 μ m) COATING ONTO ALUMINUM FOIL –
HIGHER LOADINGS AND DIFFERENT POLYPROPYLENE, in Newtons/in. (Newtons/cm.)

Temp (Deg C)	80	80	90	90	100	100	110	110N/cm	120	120	120	130	130	140	140
	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/in	cm	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/cm
Comparative – SLEP 1	NM	NM	0.212	0.08	2.258	0.89	4.576	1.80	5.104	2.01	4.979	1.96	5.115	2.01	
SLEP 1 w/ 5 percent PP 4	NM	NM	0.475	0.19	3.799	1.50	7.296	2.87	10.332	4.07	9.768	3.85	9.274	3.65	
SLEP 1 w/ 10 percent PP 4	0.239	0.09	1.46	0.57	4.724	1.86	10.91	4.30	10.518	4.14	10.54	4.15	9.753	3.84	
SLEP 1 w/ 15 percent PP 4	NM	NM	0.799	0.31	2.674	1.05	4.277	1.68	4.381	1.72	7.885	3.10	8.829	3.48	
SLEP 1 w/ 20 percent PP 4	NM	NM	0.664	0.26	1.353	0.53	3.069	1.21	3.652	1.44	4.692	1.85	7.342	2.89	
SLEP 1 w/ 25 percent PP 4	NM	NM	0.567	0.22	1.156	0.46	1.423	0.56	2.486	0.98	2.253	0.89	2.554	1.01	
SLEP 1 w/ 5 percent PP 1	0.25	0.10	2.189	0.86	4.475	1.76	11.39	4.48	10.624	4.18	10.63	4.19	9.09	3.58	
SLEP 1 w/ 10 percent PP 1	0.241	0.09	1.882	0.74	5.695	2.24	11.83	4.66	12.275	4.83	11.26	4.43	9.681	3.81	
SLEP 1 w/ 15 percent PP 1	NM	NM	0.652	0.26	2.718	1.07	7.047	2.77	8.523	3.36	10.45	4.11	9.546	3.76	

NM denotes not measurable.

TABLE 7, continued

HOT TACK DATA FOR 1 MIL (25 μ m) COATING ONTO ALUMINUM FOIL –
HIGHER LOADINGS AND DIFFERENT POLYPROPYLENE, in Newtons/in. (Newtons/cm.)

Temp (Deg C)	150 N/in	150 N/cm	170 N/in	170 N/cm	190 N/in	190 N/cm	210 N/in	210 N/cm
Comparative	4.356	1.71	3.561	1.40	3.37	1.33	2.346	0.92
- SLEP 1								
SLEP 1 w/ 5	6.786	2.67	4.65	1.83	4.438	1.75	4.559	1.79
percent PP 4								
SLEP 1 w/	7.353	2.89	5.886	2.32	5.288	2.08	5.155	2.03
10 percent								
PP 4								
SLEP 1 w/	7.291	2.87	5.366	2.11	1.44	0.57	NM	NM
15 percent								
PP 4								
SLEP 1 w/	6.94	2.73	4.653	1.83	0.955	0.38	NM	NM
20 percent								
PP 4								
SLEP 1 w/	3.34	1.31	3.647	1.44	0.663	0.26	NM	NM
25 percent								
PP 4								
SLEP 1 w/ 5	7.369	2.90	5.801	2.28	6.503	2.56	6.089	2.40
percent PP 1								
SLEP 1 w/	9.464	3.73	7.154	2.82	6.938	2.73	6.879	2.71
10 percent								
PP 1								
SLEP 1 w/	7.145	2.81	6.173	2.43	3.633	1.43	2.398	0.94
15 percent								
PP 1								

NM denotes not measurable.

TABLE 8

HOT TACK DATA FOR 1 MIL (25 μ m) COATING ONTO PAPER –
VARIOUS MELT INDEX AND DENSITY POLYMERS, in Newtons/in. (Newtons/cm.)

Temp (Deg C)	60	80	80	100	100	120	120N/	140	140
	N/in	N/cm	N/in	N/in	N/cm	N/in	cm	N/in	N/cm
Comparative	0.21	0.08	0.263	0.467	0.18	7.268	2.86	6.885	2.71
- SLEP 2 w/ 8 percent LDPE 1									
SLEP 2 W/ 5 percent PP 1 & 8 percent LDPE 1	0.446	0.18	0.465	0.72	0.28	6.313	2.49	8.759	3.45
SLEP 4 W/ 8 percent LDPE 1	0.361	0.14	0.365	0.257	0.10	3.45	1.36	2.159	0.85
SLEP 4 W/ 5 percent PP 1 & 8 percent LDPE 1	0.627	0.25	0.738	0.454	0.18	5.147	2.03	4.884	1.92
Comparative – Exact 3139 w/ 8 percent LDPE 1	0.448	0.18	0.481	0.44	0.17	0.229	0.09	0.774	0.30
Exact 3139 w/ 5 percent PP 1 and 8 percent LDPE 1	0.355	0.14	0.43	0.251	0.10	2.842	1.12	8.402	3.31

TABLE 8, continued

HOT TACK DATA FOR 1 MIL (25 μ m) COATING ONTO PAPER –
VARIOUS MELT INDEX AND DENSITY POLYMERS, in Newtons/in. (Newtons/cm.)

Temp (Deg C)	160 N/in	160 N/cm	180 N/in	180 N/cm	200 N/in	200 N/cm
Comparative - SLEP 2 w/ 8 percent LDPE 1	5.285	2.08	4.134	1.63	3.472	1.37
SLEP 2 W/ 5 percent PP 1 & 8 percent LDPE 1	7.375	2.90	6.037	2.38	4.653	1.83
SLEP 4 W/ 8 percent LDPE 1	4.547	1.79	3.874	1.53	3.459	1.36
SLEP 4 W/ 5 percent PP 1 8 percent LDPE 1	5.071	2.00	4.193	1.65	3.926	1.55
Comparative - Exact 3139 w/ 8 percent LDPE 1	1.338	0.53	1.825	0.72	0.744	0.29
Exact 3139 w/ 5 percent PP 1 and 8 percent LDPE 1	8.053	3.17	7.251	2.85	5.739	2.26

TABLE 9

HOT TACK DATA FOR 1 MIL (25 μ m) COATING ONTO PAPER – NO LDPE IN LEP, in Newtons/in. (Newtons/cm.)

Temp (Deg C)	90	100	100	110	110	120	120N/c	130	130	140	140	150	150
	N/in	N/cm	N/in	N/cm	N/in	N/in	m	N/in	N/cm	N/in	N/cm	N/in	N/cm
Comparative - SLEP 3	0.13	0.05	0.324	0.13	2.396	0.94	2.379	0.94	2.478	0.98	2.395	0.94	NM
SLEP 3 W/ 5 percent PP 1	0.176	0.07	2.16	0.85	6.697	2.64	10.955	4.31	9.756	3.84	6.987	2.75	5.958
													2.35

TABLE 10

HOT TACK DATA FOR 1 MIL (25 μ m) COATING ONTO PAPER – LDPE ONLY, in Newtons/in. (Newtons/cm.)

Temp (Deg C)	100	100	110	110	120	120N/c	130	130	140	140	150	150	170	170
	N/in	N/cm	N/in	N/cm	N/in	m	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/in	N/cm
Comparative - LDPE 2	NM	NM	0.163	0.06	0.144	0.06	1.19	0.47	2.327	0.92	2.687	1.06	NM	NM
LDPE 2 W/ 5 percent PP 1	NM	NM	0.154	0.06	2.277	0.90	7.608	3.00	8.606	3.39	7.613	3.00	5.864	2.31
Comparative - LDPE 3	NM	NM	0.139	0.05	1.199	0.47	4.319	1.70	4.252	1.67	3.964	1.56	3.129	1.23
LDPE 3 W/ 5 percent PP 1	0.18	0.07	1.582	0.62	5.906	2.33	8.552	3.37	8.041	3.17	7.086	2.79	5.594	2.20
Comparative - LDPE 4	0.168	0.07	0.156	0.06	2.613	1.03	5.489	2.16	4.305	1.69	3.484	1.37	NM	NM
LDPE 4 W/ 5 percent PP 1	0.147	0.06	1.147	0.45	5.919	2.33	8.521	3.35	7.044	2.77	6.247	2.46	NM	NM

NM denotes not measurable.

TABLE 11

HOT TACK DATA FOR 1 MIL (25 μ m) COATING ONTO PAPER – EAA COPOLYMER, in Newtons/in. (Newtons/cm.)

Temp (Deg C)	90	90	100	100	100	110	110	120	120N/c	130	130	140	140	150	150	170	170
	N/in	N/cm	N/in	N/cm	N/in	N/in	N/cm	N/in	m	N/in	N/cm	N/in	N/cm	N/in	N/cm	N/in	N/cm
Comparative	0.129	0.05	0.163	0.06	3.015	1.19	8.762	3.45	11.117	4.38	10.606	4.18	9.616	3.79	6.75	2.66	
- EAA 1																	
EAA 1 W/ 5	NM	NM	0.142	0.06	2.111	0.83	10.571	4.16	12.15	4.78	13.992	5.51	13.405	5.28	10.813	4.26	
percent PP 1																	

NM denotes not measurable

TABLE 12

HOT TACK DATA FOR 1 MIL (25 μ m) COATING ONTO PAPER – VARIOUS MELT FLOW POLYPROPYLENES,
in Newtons/in. (Newtons/cm.)

Temp (Deg C)	80	80	80	90	90	90	100	100	100	110	110	120	120N/c
	N/in	N/cm	N/in	N/in	N/cm	N/in	N/in	N/cm	N/in	N/in	N/cm	N/in	m
SLEP 1 w/ 5	0.645	0.25	1.977	0.78	10.44	3.695	1.45	12.533	4.93				
percent PP 1													
SLEP 1 w/ 5	0.167	0.07	0.133	0.05	5.129	0.984	0.39	8.601	3.39				
percent PP 3													
SLEP 1 w/ 5	0.154	0.06	0.199	0.08	6.2	2.014	0.79	9.108	3.59				
percent PP 2													

TABLE 12, continued

Temp (Deg C)	130 N/in	130 N/cm	140 N/in	140 N/cm	150 N/in	150 N/cm	160 N/in	160 N/cm	170 N/in	170 N/cm
SLEP 1 w/ 5 percent PP 1	12.743	5.02	11.697	4.61	10.575	4.16	9.3765	3.69	8.178	3.22
SLEP 1 w/ 5 percent PP 3	9.338	3.68	6.657	2.62	5.394	2.12	4.883	1.92	3.519	1.39
SLEP 1 w/ 5 percent PP 2	8.324	3.28	6.72	2.65	7.104	2.80	5.246	2.07	3.381	1.33

TABLE 13

HOT TACK DATA FOR 1 MIL (25 μ m) COATING ONTO PAPER –
LOWER PERCENTAGE POLYPROPYLENE, in Newtons/in. (Newtons/cm.)

Temp (Deg C)	80	80- N/in	100	100 N/cm	120	120 N/cm	140	140 N/cm	160	160N/c m	180	180 N/cm	200	200 N/in
Comparative – SLEP 1	0.213	0.08	0.22	0.559	2.44	6.185	4.913	1.93	0.81	2.065	2.221	0.87	0.5	0.20
SLEP1 W/1 percent PP 1	0.201	0.08	0.41	1.038	2.88	7.306	5.647	2.22	1.43	3.625	1.831	0.72	0.659	0.26
SLEP1 W/2 percent PP 1	0.158	0.06	0.63	1.593	3.74	9.499	5.604	2.21	1.71	4.348	2.464	0.97	2.521	0.99
SLEP1 W/3 percent PP 1	0.276	0.11	1.16	2.955	8.13	8.13	5.48	2.16	1.73	4.403	3.115	1.23	3.291	1.30
SLEP1 W/4 percent PP 1	0.447	0.18	2.42	6.138	9.294	9.294	6.644	2.62	2.19	5.57	5.348	2.11	6.201	2.44
SLEP1 W/5 percent PP 1	1.012	0.40	2.08	5.293	9.593	9.593	6.457	2.54	1.96	4.967	5.057	1.99	5.294	2.08

TABLE 14

HOT TACK DATA FOR 1 MIL (25 μ m) COATING ONTO PAPER –
MODIFICATION OF A ZIEGLER-NATTA POLYMERIZED LEP, in Newtons/in. (Newtons/cm.)

Temp (Deg C)	130	130 N/in	140	140 N/cm	150	150 N/in	160	160 N/cm	170	170 N/in
Comparative – LEP 1	0.273	0.11	0.21	0.529	1.584	0.62	1.00	2.528	1.911	0.75
LEP 1 w/5 percent PP 1	1.123	0.44	1.98	5.019	8.998	3.54	3.76	9.552	7.365	2.90

WHAT IS CLAIMED IS:

- 5 1. A heat-sealable film layer comprising:
- (a) from 2 to 13 percent by weight of polypropylene which is a homopolymer or copolymer comprising at least about 93 percent propylene and less than about 8 percent alpha-olefin based on the weight of the polymer, and which has a melt flow rate of from 1.0 to 50 dg/minute as measured in accordance with ASTM D-1238, Condition 230° C/2.16 kg;
- 10 (b) from 87 to 98 percent by weight of a polymer selected from the group consisting of linear ethylene polymer, substantially linear ethylene polymer, low density ethylene polymer, and mixtures thereof;
- 15 wherein the linear ethylene polymer and substantially linear ethylene polymer are characterized by:
- (1) a density of from 0.87 to 0.96 g/cm³,
- (2) a molecular weight distribution, M_w/M_n of less than or equal to about 5,
- 20 (3) a melt index, I_2 , as measured in accordance with ASTM D-1238, Condition 190° C/2.16 kg of from 0.5 to 20.0 dg/minute; and
- wherein the low density ethylene polymer is characterized by:
- (1) a density of from 0.91 to 0.96 g/cm³, and
- 25 (2) a melt index, I_2 , as measured in accordance with ASTM D-1238, Condition 190° C/2.16 kg of from 0.1 to 20.0 dg/minute.
2. The layer of Claim 1 wherein the low density polyethylene comprises low density polyethylene produced by a free radical polymerization.
- 30 3. The layer of Claim 1 wherein the linear ethylene polymer or substantially linear ethylene polymer comprises a copolymer of ethylene and 1-octene, ethylene and 1-butene,

ethylene and 1-hexene, ethylene and 1-pentene, ethylene and 1-heptene, or ethylene and 4-methylpentene-1.

4. The layer of Claim 1 which comprises from 67 to 93 percent by weight linear
5 ethylene polymer, substantially linear ethylene polymer or a mixture thereof and from 5 to 20 percent by weight low density polyethylene.

5. The layer of Claim 1 which comprises from 4 to 10 percent by weight
polypropylene.

10

6. The layer of Claim 5 wherein the polypropylene is a homopolymer.

7. The layer of Claim 1 which comprises from 80 to 90 percent by weight linear
ethylene polymer or substantially linear ethylene polymer and wherein said linear
15 ethylene polymer or substantially linear ethylene polymer is a copolymer of ethylene and 1-octene.

8. The layer of Claim 7 wherein the composition has a melt index, I_2 , as measured in
accordance with ASTM D-1238, Condition 190° C/2.16 kg of from 4.0 to 20.0 dg/minute.

20

9. The layer of Claim 7 wherein the composition has a density of from 0.890 to
0.910 g/cm³.

10. A composition comprising:

25

- (a) from 2 to 13 percent by weight of polypropylene which is a homopolymer
or a copolymer derived from at least about 80 percent propylene monomer and
less than about 20 percent alpha-olefin monomer based on the total weight of
the monomers, and which has a melt flow rate of from 1.0 to 50 dg/minute as
30 measured in accordance with ASTM D-1238, Condition 230° C/2.16 kg.

- (b) from 87 to 98 percent by weight of a polymer selected from the group consisting of linear ethylene polymer, substantially linear ethylene polymer, low density ethylene polymer and mixtures thereof;

5 wherein the linear ethylene polymer and substantially linear ethylene polymer is characterized by:

- (1) a density of from 0.87 to 0.960 g/cm³,
- (2) a molecular weight distribution, M_w/M_n of less than or equal to about 5, and
- 10 (3) a melt index, I_2 , as measured in accordance with ASTM D-1238, Condition 190° C/2.16 kg of from 0.5 to 20.0 dg/minute; and

wherein the low density ethylene polymer is characterized by:

- (1) a density of from 0.91 to 0.96 g/cm³, and
- 15 (2) a melt index, I_2 , as measured in accordance with ASTM D-1238, Condition 190° C/2.16 kg of from 0.1 to 20.0 dg/minute.

- 11. The composition of Claim 10 wherein the low density ethylene polymer is low density polyethylene produced by a free radical polymerization.
- 20 12. The composition of Claim 10 wherein the linear ethylene polymer or substantially linear ethylene polymer is a copolymer of ethylene and 1-octene.
- 13. The composition of Claim 10 wherein the linear ethylene polymer or substantially linear ethylene polymer is a copolymer of ethylene and 1-butene.
- 25 14. The composition of Claim 10 wherein the linear ethylene polymer or substantially linear ethylene polymer is a copolymer of ethylene and 1-hexene.
- 30 15. The composition of Claim 10 wherein the linear ethylene polymer or substantially linear ethylene polymer is a copolymer of ethylene and 1-pentene.

16. The composition of Claim 10 wherein the linear ethylene polymer or substantially linear ethylene polymer is a copolymer of ethylene and 1-heptene.

17. The composition of Claim 10 wherein the linear ethylene polymer or substantially
5 linear ethylene polymer is a copolymer of ethylene and 4-methyl-1-pentene.

18. The composition of Claim 10 which comprises from 67 to 93 percent by weight linear or substantially linear ethylene polymer and from 5 to 20 percent by weight low density polyethylene.

10

19. The composition of Claim 10 which comprises from 4 to 10 percent by weight polypropylene.

20. The composition of Claim 19 wherein the polypropylene is a homopolymer.

15

21. The composition of Claim 12 which comprises from 80 to 90 percent by weight of a copolymer of ethylene and 1-octene.

22. The composition of Claim 21 wherein the composition has a melt index, I_2 , as
20 measured in accordance with ASTM D-1238, Condition 190° C/2.16 kg of from 4 to 20 dg/minute.

23. The composition of Claim 22 wherein the composition has a density of from 0.89 to 0.91 g/cm³.

25

24. The composition of Claim 10 wherein the low density ethylene polymer is a copolymer derived from at least about 80 weight percent ethylene monomer and less than about 20 weight percent of a monomer selected from the group consisting of an acrylate, an acrylic, and an acetate.

30

25. A packaging material having improved hot tack comprising a substrate and a polymer composition coated thereon wherein the polymer composition comprises:

5 (a) from 2 to 13 percent by weight of polypropylene which is a homopolymer or a copolymer derived from at least about 93 percent propylene monomer and less than about 8 percent alpha-olefin monomer based on the weight of the monomers, and which has a melt flow rate of from 1.0 to 50 dg/minute as measured in accordance with ASTM D-1238, Condition 230° C/2.16 kg;

10 (b) from 87 to 98 percent by weight of a polymer selected from the group consisting of linear ethylene polymer, substantially linear ethylene polymer, low density ethylene polymer, and mixtures thereof;

wherein the linear ethylene polymer and substantially linear ethylene polymer are characterized by:

15 (1) a density of from 0.87 to 0.96 g/cm³,
(2) a molecular weight distribution, M_w/M_n of less than or equal to about 5,
and

(3) a melt index, I_2 , as measured in accordance with ASTM D-1238, Condition 190° C/2.16 kg of from 0.5 to 20.0 dg/minute; and

20

wherein the low density ethylene polymer is characterized by:

(1) a density of from 0.91 to 0.96 g/cm³, and
(2) a melt index, I_2 , as measured in accordance with ASTM D-1238, Condition 190° C/2.16 kg of from 0.1 to 20.0 dg/minute.

25

26. The packaging material of Claim 25 wherein the substrate is selected from the group consisting of papers, foils, oriented polypropylenes, polyamides, polyesters, polyethylenes, polyethylene terephthalate, and metallized substrates.

30 27. The packaging material of Claim 25 wherein the linear ethylene polymer or substantially linear ethylene polymer is selected from the group consisting of a copolymer

of ethylene and 1-octene, ethylene and 1-butene, ethylene and 1-hexene, ethylene and 1-pentene, ethylene and 1-heptene, and ethylene and 4-methyl-1-pentene.

28. The packaging material of Claim 27 wherein the polymer composition comprises
5 from 67 to 93 percent by weight linear ethylene polymer or substantially linear ethylene polymer and from 5 to 20 percent by weight low density polyethylene.

29. The packaging material of Claim 28 wherein the polymer composition comprises from 4 to 10 percent by weight polypropylene.

10

30. The packaging material of Claim 29 wherein the polypropylene is a homopolymer.

31. The packaging material of Claim 25 wherein the polymer composition is coextruded onto the substrate.

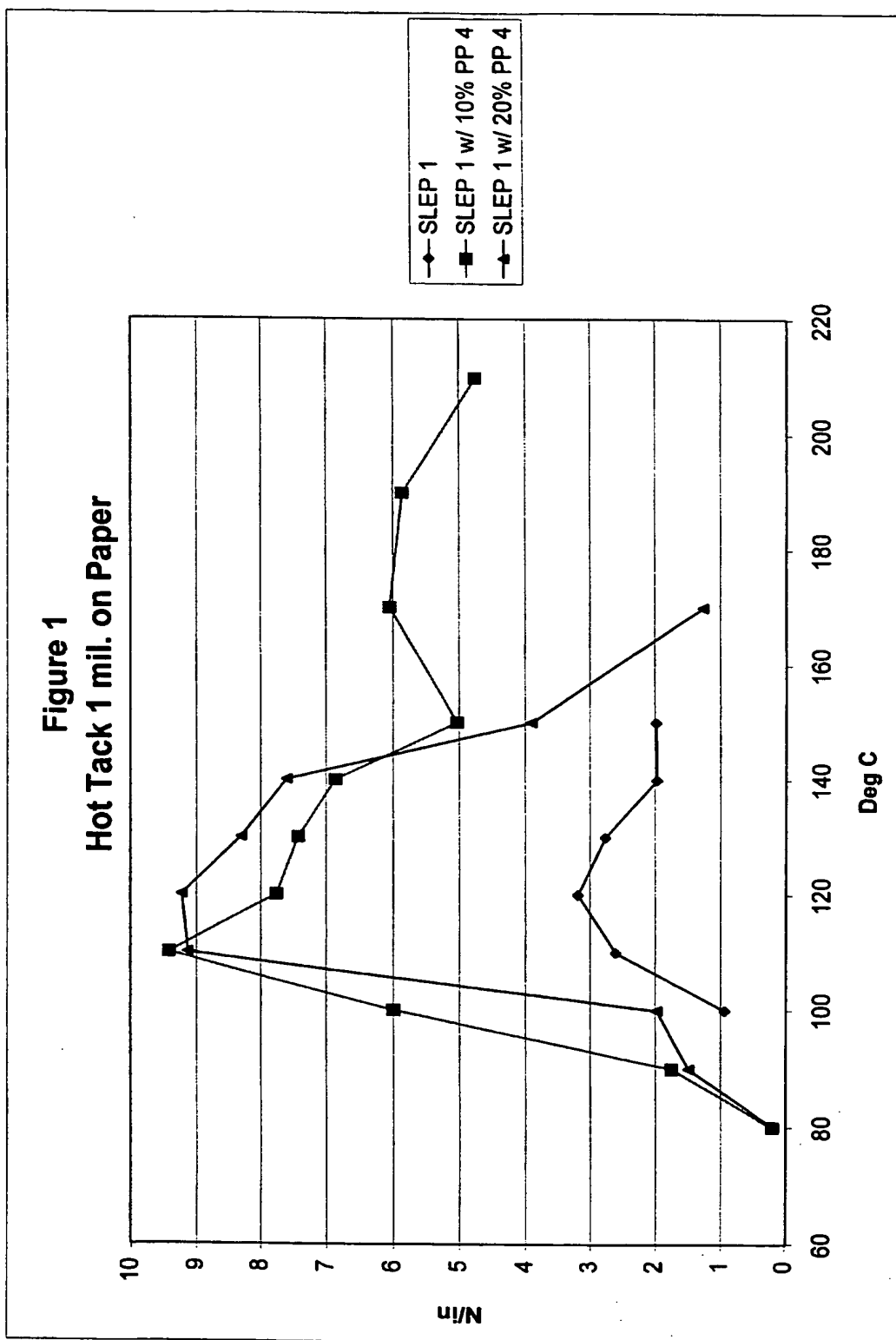


Figure 2
Hot Tack 1 mil on Foil

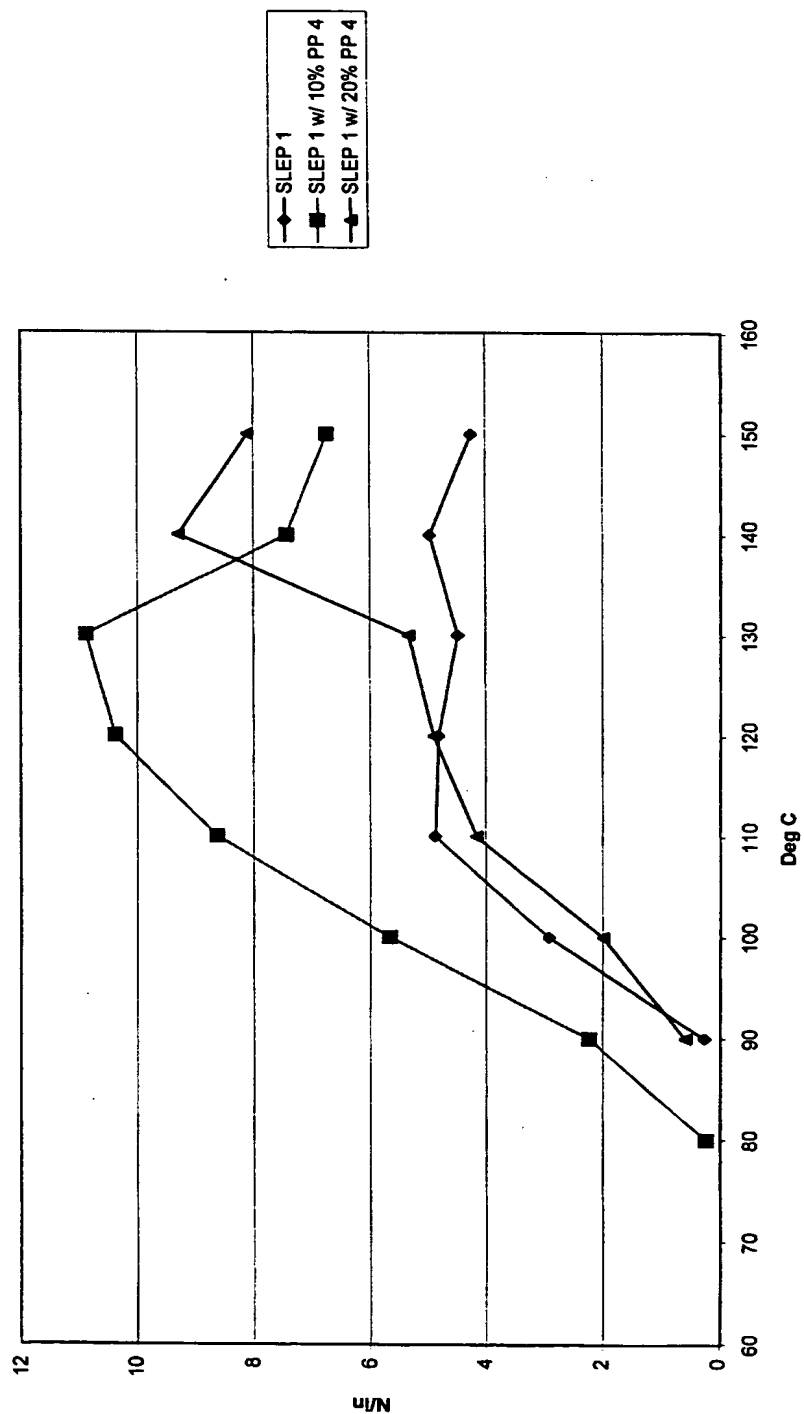


Figure 3
Hot Tack on Industrial Grade Polypropylene 1 mil

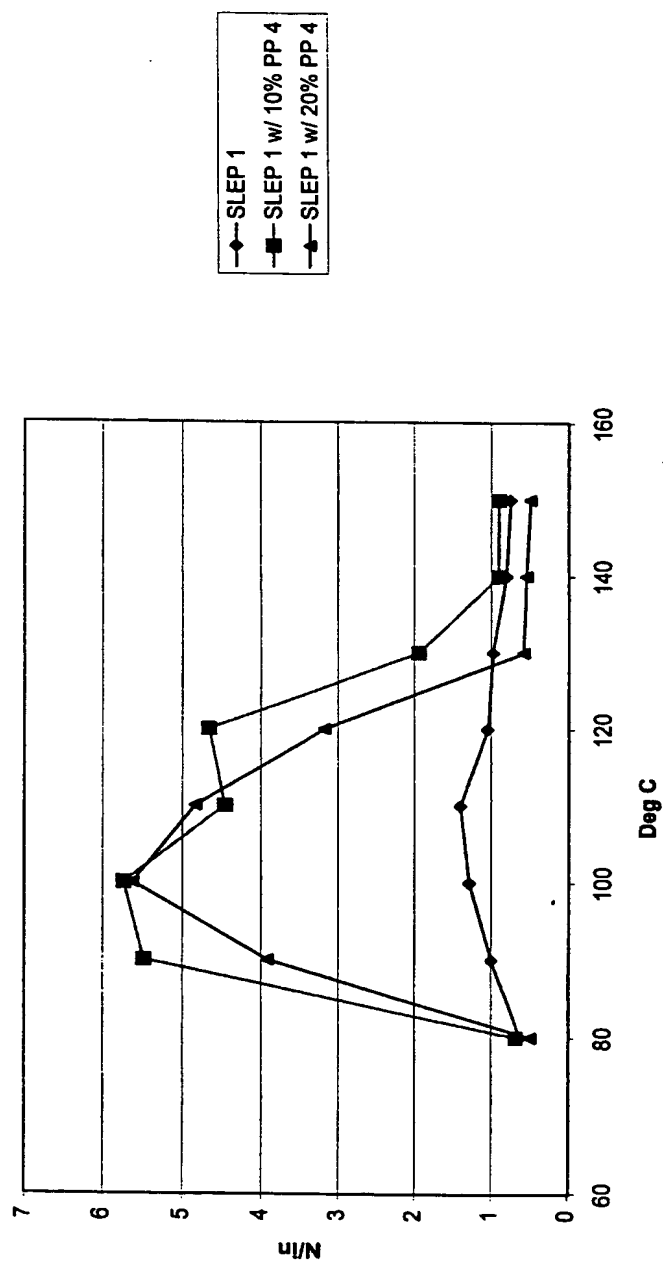
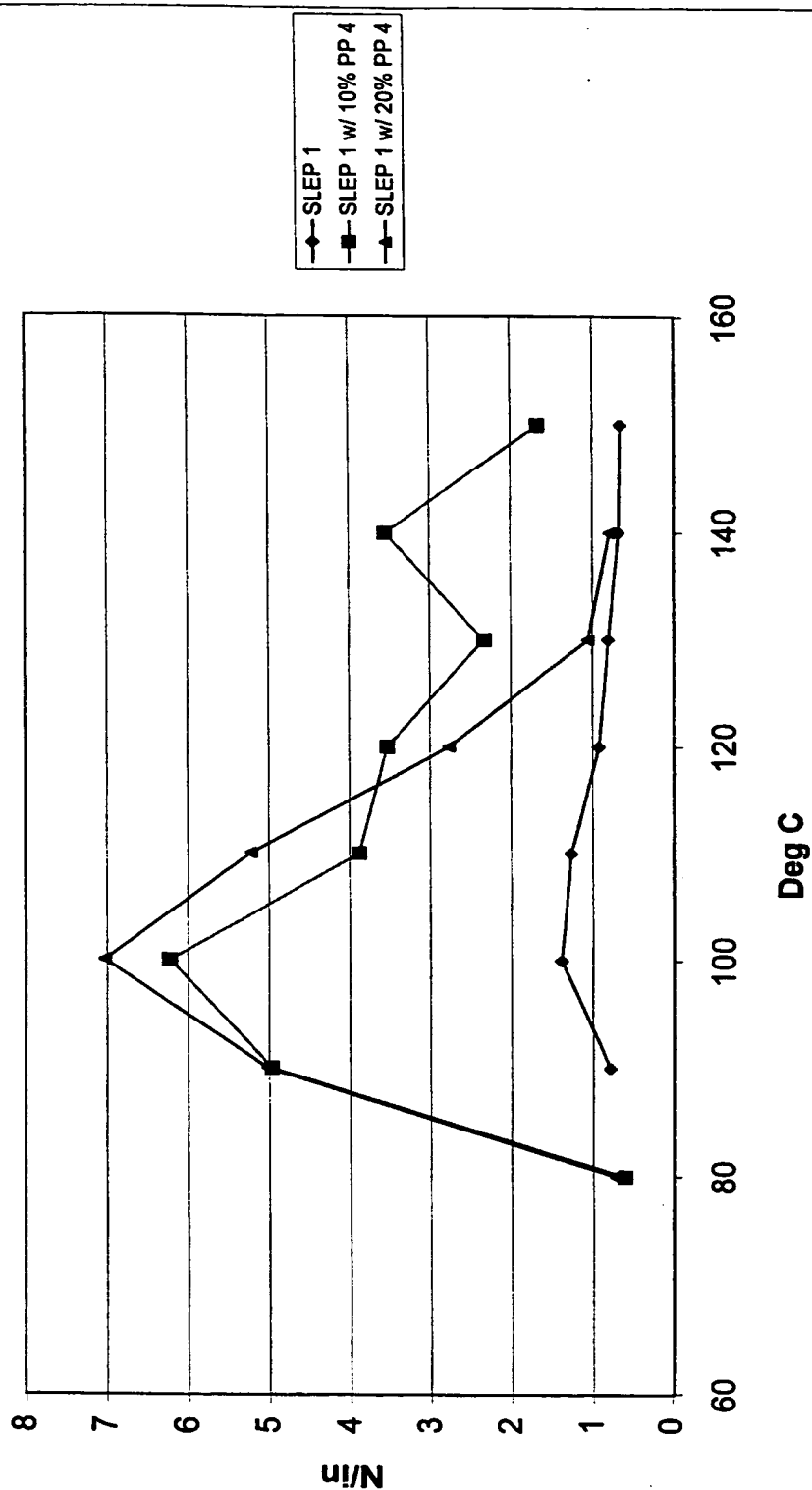


Figure 4
Hot Tack 1 mil on PET film



INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 00/16587

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08L23/04 C08L23/06 C08L23/08		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 321 220 A (MITSUI PETROCHEMICAL IND) 21 June 1989 (1989-06-21) abstract; claims 1-10 page 2, line 50 page 3, line 5,17; table 1 page 2, line 57 page 4, line 18 ---	1-8, 10-22, 25-31
X	WO 98 37139 A (LOON ACHIEL JOSEPHUS MARIA VAN ;EXXON CHEMICAL PATENTS INC (US)) 27 August 1998 (1998-08-27) abstract; claims 1-18 page 1, line 5-10 page 4, line 24,25 page 5, line 23,24 page 7, line 25 page 12, line 4 ---	1-31
-/--		
☒ Further documents are listed in the continuation of box C.		
☒ Patent family members are listed in annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 15 September 2000		Date of mailing of the international search report 06/10/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Bergmans, K

INTERNATIONAL SEARCH REPORT

Inter- national Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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P,X	WO 00 02960 A (ANIBALDI REMO ;CIARAFONI MARCO (IT); COLLINA GIANNI (IT); COVEZZI) 20 January 2000 (2000-01-20) abstract; claims 1-7 page 3, line 9 page 4, line 4 page 5, line 1-26 page 7, line 16 page 10, line 13-16 ----	1-31
A	EP 0 186 279 A (MOBIL OIL CORP) 2 July 1986 (1986-07-02) abstract; claims 1-14 page 3, column 3, line 30 -----	1-31

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(54) Title: HOT-MELT COMPOSITION AND MODIFIED AROMATIC PETROLEUM RESIN FOR USE THEREIN

(54) 発明の名称: ホットメルト組成物およびそれに用いる変性芳香族石油樹脂

(57) Abstract: A hot-melt composition which comprises specific amounts of: (a) an ethylene copolymer resin; (b) a modified aromatic petroleum resin with a specific weight-average molecular weight obtained by copolymerizing (1) a polymerizable ingredient contained in a fraction resulting from the thermal cracking of petroleum hydrocarbons having a specific boiling point range, a specific vinyltoluene content, and a specific indene content, (2) β -phellandrene or turpentine oil containing β -phellandrene, and (3) a phenol compound in a specific proportion with the aid of a Friedel-Crafts catalyst; and (c) a wax. The composition has excellent thermal stability and improved high-temperature bonding properties. It is usable in a hot-melt coating material, printing ink, adhesive, sealant, etc.

(57) 要約:

(a) エチレン系共重合樹脂、(b) (1) 特定の沸点範囲、ビニルトルエン含有率およびインデン含有率を有する石油系炭化水素類の熱分解により得られる熱分解油留分の重合可能成分、(2) β -フェランドレンまたは β -フェランドレン含有テレピン油および(3) フェノール化合物を特定割合でフリーデルクラフツ型触媒を用いて共重合した特定の重量平均分子量の変性芳香族石油樹脂および(c) ワックスを特定量配合したホットメルト組成物である。本組成物は、熱安定性に優れ、耐熱接着性が改善され、ホットメルト型の塗料、印刷インキ、接着剤またはシーラントなどとして用いることができる。

WO 02/18510 A1

明細書

ホットメルト組成物およびそれに用いる変性芳香族石油樹脂

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技術分野

本発明は、ホットメルト組成物およびそれに用いる変性芳香族石油樹脂に関し、特に、ホットメルト接着剤として、例えば熱安定性と耐熱接着性が改善されたホットメルト組成物、およびそれに用いるホットメルト組成物用変性芳香族石油樹脂に関するものである。

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背景技術

ホットメルト組成物としては、特開昭55-65248号公報では、インデン含有率が低くかつビニルトルエン含有率の高い特定の熱分解油留分にフェノール類とテレピン油とを共重合させて得られる変性芳香族石油樹脂を配合することが

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提案されている。
この変性芳香族石油樹脂は、エチレン-酢酸ビニル共重合体（以下、「EVA」と称す）等のベース樹脂との相溶性などが優れており、EVA等と配合して用いられるホットメルト接着剤に好適な石油樹脂である。しかしながら、このホットメルト接着剤は一定温度以上の領域における実用的な接着力が必ずしも充分では

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なかった。
例えば、製造工程から供給される各種の高温液体を缶、瓶など適宜の容器に充填し、さらにこれらをまとめて段ボール箱等に梱包するような包装作業においては、内容物の熱が包装箱に伝わる。前記公報に記載されているように、一般に固化により接着力が発現するホットメルト接着剤には高温の環境下で、接着力が低下し易い。したがって、内容物が充分冷却され包装箱が充分低い温度になるまで放置せざるを得ないため、放置時間分だけ包装の生産速度が低下することになる。それ故、各種基材、特に段ボール紙等の紙基材における耐熱接着性の向上が望まれている。耐熱接着性の向上には、一般には石油樹脂の分子量を増大させることが有効と考えられる。しかしながら単なる分子量の増大は、接着特性、特に低温

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接着性の低下を招きやすい。

本発明は、前記公報に記載された変性芳香族石油樹脂が有する、特にEVA等との組成物とした場合の低温接着性の良好なホットメルト接着剤特性を保持しつつ、その耐熱接着性や熱安定性の改善されたホットメルト組成物用の石油樹脂を
5 提供することを課題とするものである。

発明の開示

以下、本発明について詳細に説明する。

本発明者らは、前記のような問題点について鋭意研究した結果、芳香族石油樹脂を重合する際に、特定割合のインデンやビニルトルエンを含有する熱分解油留分を用い、かつβ-フェランドレンおよびフェノール化合物を選択することにより前記課題が解決できることを見出した。

すなわち、本発明の第1は、

(a) エチレン系共重合樹脂 100重量部、
15 (b) 次の(1)～(3)をフリーデルクラフツ型触媒の存在下に共重合してなる重量平均分子量500～2000の範囲にある変性芳香族石油樹脂
50～150重量部、

(1) 沸点が140～220℃の範囲にある成分を主とし、ビニルトルエン含有率が10%以上60%未満、インデン含有率が10～80%である石油系炭化
20 水素類の熱分解により得られる熱分解油留分の重合可能成分100重量部、

(2) β-フェランドレン3～40重量部、

(3) フェノール化合物1～15重量部、および、

(c) ワックス 10～100重量部

からなることを特徴とするホットメルト組成物に関する。

25 本発明の第2は、本発明の第1における(1)熱分解油留分が、さらに共役ジオレフィン含有率が2.0%以下であるホットメルト組成物に関する。

本発明の第3は、β-フェランドレンを15重量%以上含み、かつ、熱分解油留分の重合可能成分100重量部に対しβ-フェランドレンの量が3～40重量部に相当する量の(2-1)テレピン油を用いる第1の発明に記載のホットメル

ト組成物に関する。

本発明の第4は、前記第3の発明において、(1)熱分解油留分中の共役ジオレフィン含有率が2.0%以下であるホットメルト組成物に関する。

5 本発明の第5は、前記第1あるいは第4の発明におけるエチレン系共重合樹脂が、エチレン-酢酸ビニル共重合体であるホットメルト組成物に関する。

本発明の第6は、(1)石油系炭化水素類の熱分解により得られる熱分解油留分で、沸点が140～220℃の範囲にある成分を主とし、ビニルトルエン含有率が10%以上60%未満、インデン含有率が10～80%であり、その重合可能成分100重量部に対し、(2)β-フェランドレン3～40重量部および

10 (3)フェノール化合物1～15重量部をフリーデルクラフツ型触媒の存在下に共重合してなる重量平均分子量500～2000の範囲にあるホットメルト組成物用変性芳香族石油樹脂に関する。

以下、本発明をさらに説明する。

本発明のホットメルト組成物の(a)エチレン系共重合樹脂としては、エチレンと共重合可能な極性単量体、例えば、酢酸ビニルなどのモノカルボン酸ビニル
15 エステル、アクリル酸、メタクリル酸およびそれらのメタノール、エタノールなどのアルコールなどとのエステルの一種または二種以上の共重合体が例示される。

エチレン系共重合樹脂中の極性単量体成分の含有量は、1～60重量%、好ましくは15～45重量%であるものが適当である。分子量の目安として用いられているメルトインデックス(190℃、荷重2.16Kg、10分間にて測定)
20 は10～1000g/10分であるものが好ましい。より好ましいエチレン系共重合樹脂の例としてEVA、エチレン-エチルアクリレート共重合体などがある。

本発明において使用する(b)変性芳香族石油樹脂の原料の(1)熱分解油留分は、原油、灯油、ナフサ、ブタン等の石油系炭化水素類の熱分解により得られ、かつ沸点140～220℃の範囲にある成分を主とする留分であって、ビ
25 ニルトルエン含有率が10%以上60%未満、好ましくは10%以上55%以下、インデン含有率が10～80%、好ましくは15～80%である。好ましくはさらに共役ジオレフィン含有率が2.0%以下である。

通常、熱分解油留分は、重合可能成分と非重合可能成分とからなる。

重合可能成分は、熱分解油留分中、上記の沸点範囲に含まれる成分のうち重合可能な不飽和成分であり、例えばスチレン、そのアルキル誘導体である α -メチルスチレンや β -メチルスチレン、ビニルトルエン；インデン、そのアルキル誘導体；シクロペンタジエン、メチルシクロペンタジエン、ジシクロペンタジエン
5 とそのアルキル誘導体などである。またこれら重合可能成分は、熱分解油留分中に通常10～90重量%存在する。

非重合可能成分は熱分解油留分中の残余の成分からなり、炭素数が9個のアルキルベンゼン（C₉アルキルベンゼン）などの主として飽和の炭化水素化合物であり本発明においては主として溶剤の働きをなす。

10 なお、石油樹脂の製造に際しては、粘度調整、その他の目的のために適宜に別途非重合成分としてのC₉アルキルベンゼンなどの飽和炭化水素化合物を加えるなどにより重合可能成分の含有率を、 β -フェランドレン、場合により β -フェランドレン含有テレピン油やフェノール化合物等も含めた全張り込み量に対して30～70重量%とするなどにより重合の調整をすることができる。

15 ここで、ビニルトルエン含有率（%）は、上記熱分解油留分中に含まれる成分のうち重合可能成分量（重量%）に対するビニルトルエンの含有量（重量%）の割合をいう。インデン含有率（%）は、同じく上記熱分解油留分中に含まれる成分のうち重合可能成分量（重量%）に対するインデンおよびそのアルキル誘導体の合計含有量（重量%）の割合をいう。また、共役ジオレフィン含有率（%）と
20 は、上記熱分解油留分中に含まれる成分のうち重合可能成分量（重量%）に対するシクロペンタジエンおよびメチルシクロペンタジエンの合計含有量（重量%）の割合をいう。またビニルトルエン含有率、インデン含有率および共役ジオレフィン含有率の合計は、20%以上100%未満となる。

25 なお、各成分の含有量は、常法によりガスクロマトグラフ法により分析することができ、その結果からそれぞれの含有率を計算する。

本発明においては、熱分解油留分として沸点140～220℃の範囲にある成分を主とする留分を原料とする。沸点が140℃未満の成分は、共役ジオレフィン、非共役ジオレフィンを多量に含み、得られる樹脂の色相、耐熱安定性が悪いものであるために好ましくない。また、220℃を越える沸点の成分を用いると

同様に耐熱安定性、色相が十分とはいえない樹脂が得られ、そのうえホットメル
ト接着剤にしたときの接着性も劣ったものとなるので好ましくない。

さらにビニルトルエンおよびインデン含有率を、本発明で規定する上記範囲に
することが肝要であり、このようにすることにより、得られる樹脂を用いるホッ
5 トメルト組成物の耐熱接着性を向上させることができる。

また前記（１）熱分解油留分は、共役ジオレフィン含有率が２．０％以下のもの
が好ましい。共役ジオレフィン含有率は、例えば熱分解油留分を蒸留すること
により調整することができる。また必要に応じて、熱分解油留分のジシクロペン
タジエンやジメチルシクロペンタジエンなどが熱分解してシクロペンタジエンや
10 メチルシクロペンタジエンが生成しないように、ジシクロペンタジエンなどの熱
分解温度以下で蒸留し共役ジオレフィン含有量を調整することもできる。これら
の含有率が２．０％を超えると得られる樹脂の色相や耐熱安定性が劣る等の懸念
がある。

本発明の原料である（１）熱分解油留分は、石油系炭化水素の熱分解の際に副
15 生する熱分解油を沸点１４０～２２０℃の範囲にある成分を主とするよう、通常
の工業的蒸留のみで容易に得られ、特に精密蒸留や多段蒸留をする必要はない。
しかしながらもちろん適宜にこのような精密蒸留、多段蒸留をすることにより得
ることもできる。

上記熱分解油留分中のビニルトルエンおよびインデンの含有率が所定の割合で
20 あればそのまま用いることができる。また、熱分解油留分を蒸留することにより
ビニルトルエンやインデン含有率の異なる留分を別途に調整し、これらを混合す
ることにより含有率を調整することができる。またビニルトルエンやインデンを
別途に用意し上記熱分解油留分に混合することにより任意に含有率を調整するこ
ともできる。これらの未調整あるいは調整した留分は、単独でも２種以上の混合
25 物でも使用できる。このようにしてさまざまな含有率をもった留分を調製するこ
とが可能である。この留分を原料に用いることにより、任意の含有率をもった樹
脂を製造することができ、必要に応じて樹脂の性状を調整することができる。

本発明の（ｂ）変性芳香族石油樹脂の原料である（２） β -フェランドレンは
モノテルペン炭化水素であり、天然には、ダイウイキョウ油、セリ科の一種の種

子の精油、ショウガ油、サンショウ油、テレピン油、カナダバルサム油などに存在する。その存在比は植物の種類や産地により大きく異なる。 β -フェランドレンは、これら精油をそのままあるいは異性化した後、分留して得られた留分をさらに精留することにより得られる。

- 5 工業的には例えば、ガムテレピン、ウッドテレピン、サルフェートウッドテレピン、乾留ウッドテレピンなどのテレピン油を熱などにより異性化して分留することにより得ることができる。また、 β -フェランドレンを合成する方法として、例えば、 p -メンセン-1を臭素化し、アルコール性水酸化カリで処理し、得られた化合物を精留することにより得る方法が知られている。これらの方法で得られた β -フェランドレンは、すべて本発明において使用することができる。また、
10 これら以外の方法で得られたものでも差し支えない。

- 本発明における(2) β -フェランドレンは、(1)熱分解油留分の重合可能成分100重量部に対して3~40重量部使用して重合させる。3重量部未満であると得られた樹脂のベースポリマーとの相溶性が悪くなり、反対に40重量部を
15 超えると樹脂の軟化点が低下し接着性を改善できない。

- なお、本発明においては上記(2) β -フェランドレンの代りに(2-1) β -フェランドレンの含有量が15重量%以上のテレピン油を用いることも可能である。このようなテレピン油は一般に入手可能であり、 β -フェランドレンを精製しなくてもよいのでコスト的に有利である。なお β -フェランドレンの含有量
20 が15重量%未満であるテレピン油の場合は得られた樹脂のベースポリマーとの相溶性が悪くなる。

- 上記(2-1) β -フェランドレンの含有量が15重量%以上のテレピン油は、ガムテレピン、水蒸気ウッドテレピン、サルフェートウッドテレピン、乾留ウッドテレピンなどのテレピン油を熱などにより異性化して分留することにより製造
25 することができる。しかし β -フェランドレンの含有量はテレピン油の種類や製造プロセスにより大きく異なるため、すべての異性化テレピン油が使用できるわけではない。また公知のテレピン油に別途(2) β -フェランドレンを所定量配合し上記範囲に調整して使用することも可能である。

公知のテレピン油は、針葉樹に含まれる樹液の揮発成分から製造されるもので

- あり、工業的には主としてガムテレピン、水蒸気ウッドテレピン、サルフェートウッドテレピンおよび乾留ウッドテレピンの4種から製造されるものに分類される。このうちガムテレピンは、松の生木の傷口や傷跡から採取した生松ヤニを蒸留することにより得られる。水蒸気ウッドテレピンまたはウッドテレピンは、樹皮と
- 5 辺材が腐敗して脱落した未採取の松の切り株の抽出物を蒸留することにより得られる。またサルフェートウッドテレピンまたはサルフェートテレピンは、製紙用クラフト（サルフェート）パルプ化プロセスの加熱工程で発生する蒸気を凝縮することによって得られる。乾留ウッドテレピンは、樹脂分の多い樹木や伐採木などの針葉樹木廃材を、乾留（炭化）させて得られる軽出蒸留物から製造される。
- 10 通常使用されているものは更に蒸留されたものである。

- 本発明においては、さらに（3）フェノール化合物1～15重量部を、熱分解油留分の重合可能成分100重量部に対して加える。ここで、フェノール化合物とは、フェノールおよびクレゾール、キシレノールなどのアルキル置換フェノールである。これらは混合して使用することができる。加えるフェノール化合物が
- 15 1重量部未満であると、得られた樹脂のベースポリマーとの相溶性が悪くなり、反対に15重量部を超えると樹脂の軟化点が低下し、いずれも接着性を改善できない。

- 本発明の（b）変性芳香族石油樹脂の重合は、上記（1）熱分解油留分100重量部に対して（2） β -フェランドレン3～40重量部または（2-1） β -フェランドレンを15重量%以上含有したテレピン油、（3）フェノール化合物1
- 20 ～15重量部を0.05～5.0重量%のフリーデルクラフツ型触媒の存在下に行う。フリーデルクラフツ型触媒としては、塩化アルミニウム、三フッ化ホウ素ガスまたは水、エーテル類、フェノール類、アルコール類等を使用したこれらの錯体触媒、例えば、三フッ化ホウ素・フェノラートなどが好ましい。なお、錯体
- 25 触媒として含まれるフェノール化合物は通常その量は少ないのではあるが、前記（3）フェノール化合物の量にこれも含めてフェノール化合物の量とする。また硫酸、塩酸などのプロトン酸、シリカ、アルミナなどの固体酸、あるいは酸性イオン交換樹脂なども用いることができる。

重合温度、重合時間は特に限定されないが、例えば、-20～80℃の温度範

間で0.1～10時間の範囲で共重合することができる。重合後、触媒を中和除去し、適宜に蒸留等により重量平均分子量500～2000の変性芳香族石油樹脂を得る。

上記(b)変性芳香族石油樹脂の配合割合は、(a)エチレン系共重合樹脂10
5 0重量部あたり、50～150重量部の範囲である。50重量部未満では初期接着性、耐寒性、セツト性が低下しやすく、150重量部を超えると凝集力の低下に伴って接着強度も低下しやすい。

また、(c)ワックスとしては、パラフィンワックス、マイクロクリスタンワックスなどの石油系ワックス、天然ワックス、ポリエチレンワックス、ポリプロピ
10 レンワックス、アタクチックポリプロピレンワックス、サゾールワックスなどがその目的に応じ適宜利用できる。この量は、(a)エチレン系共重合樹脂100重量部あたり、10～100重量部である。10重量部未満では熔融粘度が高く作業性や基材に対する濡れ性が低下し、100重量部を超えると接着強度が低下する。

15 上記(a)エチレン系共重合樹脂、(b)変性芳香族石油樹脂および(c)ワックスは常法により混合熔融させることにより本発明のホットメルト組成物が製造できる。

本発明のホットメルト組成物は、いわゆるホットメルト型の塗料、印刷インキ、
接着剤、シーラントなどとして使用することができる。特に好ましい用途は、ホ
20 ットメルト接着剤である。ホットメルト接着剤としては紙、プラスチック、アルミニウムなどの金属などの各種基材に適用することができる。特に好ましい基材は、段ボールを初めとする紙基材である。ホットメルトシーラントとしても、木工用、製本用などに用いることができる。

なお、接着剤、シーラント等の各用途に応じて、それぞれの用途に公知の配合
25 剤、例えば、炭酸カルシウム、酸化チタン、タルクまたはクレーなどの充填剤、可塑剤、有機または無機顔料、酸化防止剤、重合禁止剤などを適宜の量配合することができる。

発明を実施するための最良の形態

次に本発明を実施例によって具体的に説明する。なお、実施例および比較例における試験方法は下記のとおりである。

(試験方法)

(1) 重量平均分子量

- 5 GPCにより石油樹脂の重量平均分子量を測定する。カラムおよび分析条件は下記のとおりである。

カラム : TSK-Gel G-4000+2000Hs

分析条件 : 温度 38℃

圧力 5.9MPa

- 10 流速 1.0ml/min

溶媒 テトラヒドロフラン (THF)

(2) 熱安定性試験

後記の所定配合で得られたホットメルト接着剤50gを100mlのビーカーに入れ、180℃、72時間加熱後、冷却固化した状態で、目視により皮張りおよび炭化物の生成状態を次に示す判断基準で判定する。

15

ここで皮張りとは、加熱処理によりホットメルト接着剤表面に発生するゲル化物であり、また炭化物とは、ビーカー下部のホットメルト接着剤に発生する黒色物である。いずれの発生もホットメルト接着剤の吐出ノズルの詰まりを誘発するため熱安定性試験では非常に重要な項目である。

20

評価 : 皮張り : ◎ 無し、○ わずかに有り、× 多い

炭化物 : ◎ 無し、○ わずかに有り、× 多い

(3) 耐熱接着性

巾25mm、長さ100mmの二枚のKライナーの段ボールBフルート(220g/m²)を試験片とし、後記する所定配合で得られたホットメルト接着剤を試験片の表面に、フルートに対して直角(巾方向)に塗付し、下記の接着条件で同様の試験片材料の裏面でフルートが平行するように張り合わせる。

25

この試験片を用いて、荷重1kg、60℃におけるせん断クリープ試験を行い、接着試験片の接合部に破壊落下が生じた時間を測定し、耐熱接着性として時間(hr)で表示する。

	接着条件：接着剤塗布温度	180℃
	接着剤塗布量	3 g/m (0.075 g/25 mm)
	オープンタイム (接着剤の固化時間)	2 sec
	圧縮荷重	2 kg
5	圧縮時間	2 sec

(4) 低温接着性

- 巾50mm、長さ100mmのKライナーの段ボールBフルート(220g/m²)を試験片とし、後記する所定配合で得られたホットメルト接着剤を試験片の表面に、フルートに対して並行(巾方向)に塗付し、前記(3)耐熱接着性の条件で試験片材料の裏面でフルートがクロスするように張り合わせる。

この試験片を、所定の低温度下において接着試験片の接合部をL字型剥離形式で破壊させたときの該剥離面の破壊状態を次の判定条件により判定する。

評価：◎ 材料破壊、○ 大部分材料破壊、△ 大部分界面破壊、
× 界面破壊

15 <実施例1>

石油類の熱分解により得られた140～220℃の沸点範囲を有する次の組成の熱分解油留分を原料油(a)とした。

	重合可能成分	70.0重量%
	シクロペンタジエンおよびメチルシクロペンタジエンの合計含有量	
20		0.3重量%
	ビニルトルエン含有量	30.1重量%
	インデンおよびそのアルキル誘導体の合計含有量	29.3重量%
	共役ジオレフィン含有率	0.4%
	ビニルトルエン含有率	43.0%
25	インデン含有率	41.9%

この原料油(a)の重合可能成分100重量部に、β-フェランドレン含有量が30重量%でリモネン含有量が60重量%であるテレピン油(t1)23重量部、フェノール5重量部を加えた後、C₉アルキルベンゼンをさらに加えて重合可能成分が50重量%(全張り込み量に対して)になるように調整し、三フツ化

ホウ素フェノラートを0.2重量%加えて20℃で3時間重合した。消石灰で触媒を中和後濾過して蒸留により未反応の油および低重合物を除去して重量平均分子量1350の樹脂(A)を得た。

- 得られた樹脂(A)を100重量部、EVA(三井・デュポンポリケミカル(株)製:商品名エバフレックス #210、酢酸ビニル含有量28重量%、メルトインデックス 400g/10分)100重量部、パラフィンワックス(日本石油(株)製:融点155°F)50重量部を約180℃で常法により溶融混合し、ホットメルト組成物を調製し、これについて熱安定性、低温接着性を試験した。

<実施例2>

- 10 石油類の熱分解により得られた140~220℃の沸点範囲を有する次の組成の熱分解油留分を原料油(b)とした。

重合可能成分	74.6重量%
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シクロペンタジエンおよびメチルシクロペンタジエンの合計含有量	
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	1.4重量%
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- | | | |
|----|------------|---------|
| 15 | ビニルトルエン含有量 | 13.0重量% |
|----|------------|---------|

	インデンおよびそのアルキル誘導体の合計含有量	50.2重量%
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	共役ジオレフィン含有率	1.9%
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	ビニルトルエン含有率	17.4%
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	インデン含有率	67.3%
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- 20 この原料油(b)の重合可能成分100重量部に、 β -フェランドレン含有量が30重量%でリモネン含有量が60重量%であるテレピン油(t1)の23重量部、フェノール5重量部を加えた後、C₉アルキルベンゼンをさらに加えて全重合可能成分が50重量%になるように調整し、実施例1と同一条件で重合を行い、重量平均分子量1550の樹脂Bを得た。

- 25 次いで、実施例1と同様にホットメルト組成物を配合し、これについてホットメルト接着剤特性を試験した。

<実施例3>

石油類の熱分解により得られた140~220℃の沸点範囲を有する次の組成の熱分解油留分を原料油(c)とした。

	重合可能成分	58.9重量%
	シクロペンタジエンおよびメチルシクロペンタジエンの合計含有量	0.3重量%
	ビニルトルエン含有量	28.7重量%
5	インデンおよびそのアルキル誘導体の合計含有量	12.6重量%
	共役ジオレフィン含有率	0.5%
	ビニルトルエン含有率	49.0%
	インデン含有率	21.4%

この原料油(c)の重合可能成分100重量部に、 β -フェランドレン含有量が40重量%でリモネン含有量が50重量%であるテレピン油(t2)の23重量部、フェノール5重量部を加えた後、C₉アルキルベンゼンをさらに加えて全重合可能成分が50重量%になるように調整し、実施例1と同一条件で重合を行い、重量平均分子量1200の樹脂Cを得た。

その後実施例1と同様にホットメルト組成物を調製し、ホットメルト接着剤特性を試験した。

<比較例1>

石油類の熱分解により得られた140～220℃の沸点範囲を有する次の組成の熱分解油留分を原料油(d)とした。

	重合可能成分	57.1重量%
20	シクロペンタジエンおよびメチルシクロペンタジエンの合計含有量	0.1重量%
	ビニルトルエン含有量	31.1重量%
	インデンおよびそのアルキル誘導体の合計含有量	5.8重量%
	共役ジオレフィン含有率	0.2%
25	ビニルトルエン含有率	54.5%
	インデン含有率	10.2%

この原料油(d)の重合可能成分100重量部に、 α -ピネン含量90重量%、 β -ピネン含量5重量%である市販テレピン油(t3)23重量部、フェノール5重量部を加えた後、C₉アルキルベンゼンをさらに加えて全重合可能成分が5

0重量%になるように調製し、実施例1と同一条件で重合を行い、重量平均分子量1050の樹脂Dを得た。

その後実施例1と同様にホットメルト組成物を調整し、ホットメルト接着剤特性を試験した。

5 <比較例2>

前記原料油留分(c)100重量部に対し、比較例1の市販テレピン油(t3)23重量部、フェノール5重量部を加えた後、C₉アルキルベンゼンをさらに加えて重合可能成分が50重量%になるように調整し、実施例1と同一条件で重合を行い、重量平均分子量1130の樹脂Eを得た。

10 次いで、実施例1と同様にホットメルト組成物を調製し、ホットメルト接着剤特性を試験した。

実施例1～3および比較例1、2における樹脂のホットメルト組成物の接着剤特性、熱安定性の試験結果を表1に示した。

15

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表 1

			実施例			比較例	
			1	2	3	1	2
変性石油樹脂原料(重量部)	(1) 分解油成分	原料油 (a)	100	—	—	—	—
		原料油 (b)	—	100	—	—	—
		原料油 (c)	—	—	100	—	100
		原料油 (d)	—	—	—	100	—
	(2) β -フェランドレン	テレピン油 t 1	23	23	—	—	—
		テレピン油 t 2	—	—	23	—	—
	市販テレピン油 t 3		—	—	—	23	23
ホットメルト組成物	(3) フェノール化合物	フェノール	5	5	5	5	5
	組成	変性芳香族石油樹脂	樹脂名	A	B	C	D
			重量平均分子量	1350	1550	1200	1050
			配合比	100	100	100	100
		EVA	配合比	100	100	100	100
		ワックス	配合比	50	50	50	50
	性状	熱安定性	皮張り	○	○	○	○
			炭化物	◎	◎	◎	◎
		耐熱接着性 (h r)		4.5	6.0	2.5	0.5
		低温接着性	10℃	◎	◎	◎	◎
			5℃	◎	◎	◎	◎
			0℃	○	○	○	○

単位： 配合比は重量部

- ここで、比較例 1 は、前記公報に記載の実施例 1 に相当する石油樹脂を用い、
- 5 また、比較例 2 は、同じく前記公報の比較例 1 に相当する石油樹脂を用いた例である。
- 表 1 より明らかなように本発明によるホットメルト組成物は、前記公報に記載の石油樹脂を用いたホットメルト組成物に比べ、段ボール紙などの紙基材に対する接着特性、特に耐熱接着性に優れ、その一方、熱安定性や低温接着性などは遜
- 10 色ない優れた性能を有している。

産業上の利用可能性

本発明のホットメルト組成物は、熱安定性に優れ、耐熱接着性が改善されたものである。本発明のホットメルト組成物は、具体的用途としてホットメルト型の塗料、印刷インキ、接着剤またはシーラントなどとして用いることができる。例
5 えば、ホットメルト接着剤とした場合には、特に段ボール紙を初めとする紙基材に適用した場合に好ましい効果を奏する。

さらに、本発明の変性芳香族石油樹脂は、上記ホットメルト用途、特にホットメルト接着剤に好適な樹脂である。

請求の範囲

1. (a) エチレン系共重合樹脂 100重量部、
(b) 次の(1)～(3)をフリーデルクラフツ型触媒の存在下に共重合してなる重量平均分子量500～2000の範囲にある変性芳香族石油樹脂
- 5 50～150重量部、
(1) 沸点が140～220℃の範囲にある成分を主とし、ビニルトルエン含有率が10%以上60%未満、インデン含有率が10～80%である石油系炭化水素類の熱分解により得られる熱分解油留分の重合可能成分100重量部、
(2) β -フェランドレン3～40重量部、
- 10 (3) フェノール化合物1～15重量部、および、
(c) ワックス 10～100重量部、
からなるホットメルト組成物。
2. 前記(1)熱分解油留分中の共役ジオレフィン含有率が2.0%以下である請求項1記載のホットメルト組成物。
- 15 3. β -フェランドレンを15重量%以上含み、かつ、熱分解油留分の重合可能成分100重量部に対し β -フェランドレンの量が3～40重量部に相当する量の(2-1)テレピン油を用いる請求項1に記載のホットメルト組成物。
4. 前記請求項3において、(1)熱分解油留分中の共役ジオレフィン含有率が2.0%以下であるホットメルト組成物。
- 20 5. 前記(a)エチレン系共重合樹脂がエチレン-酢酸ビニル共重合体である請求項1から4のいずれかに記載のホットメルト組成物。
6. (1)石油系炭化水素類の熱分解により得られる熱分解油留分で、沸点が140～220℃の範囲にある成分を主とし、ビニルトルエン含有率が10%以上60%未満、インデン含有率が10～80%であり、その重合可能成分100
- 25 重量部に対し、
(2) β -フェランドレン3～40重量部および
(3) フェノール化合物1～15重量部
をフリーデルクラフツ型触媒の存在下に共重合してなる重量平均分子量500～2000の範囲にあるホットメルト組成物用変性芳香族石油樹脂。

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/07359

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C09J123/08, 157/02, 191/06, C08L23/08, 91/06		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ C09J123/08, 157/02, 191/06, C08L23/08, 91/06		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 842984 A1 (Nippon Petrochemicals Co., Ltd.), 20 May, 1998 (20.05.98), Claims & WO 97/45484 A1 & US 6172146 A & JP 9-316294 A	1-6
A	EP 959089 A1 (Arizona Chemical Company), 24 November, 1999 (24.11.99), Claims & US 6160083 A & JP 2000-1528 A	1-6
A	JP 11-236543 A (Du Pont-Mitsui Polychemicals Company, Ltd.), 31 August, 1999 (31.08.99), Claims (Family: none)	1-6
A	US 4419497 A (Nippon Oil Company, Limited), 06 December, 1983 (06.12.83), Claims & JP 56-30454 A	1-6
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 12 October, 2001 (12.10.01)		Date of mailing of the international search report 23 October, 2001 (23.10.01)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/07359

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 55-65248 A (Nippon Oil Company, Ltd.), 16 May, 1980 (16.05.80), Claims (Family: none)	1-6
A	JP 54-131634 A (Nippon Oil Company, Ltd.), 12 October, 1979 (12.10.79), Claims (Family: none)	1-6
A	US 3865903 A (Mobil Oil Corporation), 11 February, 1975 (11.02.75), Claims (Family: none)	1-6
A	US 3937762 A (Mobil Oil Corporation), 10 February, 1976 (10.02.76), Claims & DE 2428462 A1	1-6

国際調査報告

国際出願番号 PCT/JP01/07359

A. 発明の属する分野の分類 (国際特許分類 (IPC)) Int. Cl. ⁷ C09J123/08, 157/02, 191/06, C08L23/08, 91/06		
B. 調査を行った分野 調査を行った最小限資料 (国際特許分類 (IPC)) Int. Cl. ⁷ C09J123/08, 157/02, 191/06, C08L23/08, 91/06		
最小限資料以外の資料で調査を行った分野に含まれるもの		
国際調査で使った電子データベース (データベースの名称、調査に使用した用語)		
C. 関連すると認められる文献		
引用文献の カテゴリー*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求の範囲の番号
X	EP 842984 A1 (NIPPON PETROCHEMICALS CO., LTD.), 20. 5月. 1998 (20. 05. 98), 特許請求の範囲&WO 97/45484 A1&US 6172146 A&JP 9-31629 4 A	1-6
A	EP 959089 A1 (ARIZONA CHEMICAL COMPANY), 24. 11月. 1999 (24. 11. 9 9), 特許請求の範囲&US 6160083 A&JP 2000-1528 A	1-6
A	JP 11-236543 A (三井・デュポンポリケミカル株式会社), 31. 8月. 19 99 (31. 08. 99), 特許請求の範囲 (ファミリーなし)	1-6
☒ C欄の続きにも文献が列挙されている。 ☐ パテントファミリーに関する別紙を参照。		
* 引用文献のカテゴリー 「A」 特に関連のある文献ではなく、一般的技術水準を示すもの 「E」 国際出願日前の出願または特許であるが、国際出願日以後に公表されたもの 「L」 優先権主張に疑義を提起する文献又は他の文献の発行日若しくは他の特別な理由を確立するために引用する文献 (理由を付す) 「O」 口頭による開示、使用、展示等に言及する文献 「P」 国際出願日前で、かつ優先権の主張の基礎となる出願 の日の後に公表された文献 「T」 国際出願日又は優先日後に公表された文献であって出願と矛盾するものではなく、発明の原理又は理論の理解のために引用するもの 「X」 特に関連のある文献であって、当該文献のみで発明の新規性又は進歩性がないと考えられるもの 「Y」 特に関連のある文献であって、当該文献と他の1以上の文献との、当業者にとって自明である組合せによって進歩性がないと考えられるもの 「&」 同一パテントファミリー文献		
国際調査を完了した日 12. 10. 01	国際調査報告の発送日 23.10.01	
国際調査機関の名称及びあて先 日本国特許庁 (ISA/J P) 郵便番号100-8915 東京都千代田区霞が関三丁目4番3号	特許庁審査官 (権限のある職員) 近藤 政 克 電話番号 03-3581-1101 内線 3483	4V 9734 

C (続き) . 関連すると認められる文献		
引用文献の カテゴリー*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求の範囲の番号
A	US 4419497 A(Nippon Oil Company, Limited), 6. 12月. 1983(06. 12. 83), 特許請求の範囲&JP 56-30454 A	1-6
A	JP 55-65248 A(日本石油株式会社), 16. 5月. 1980(16. 05. 80)、特許請求の範囲(ファミリーなし)	1-6
A	JP 54-131634 A(日本石油株式会社), 12. 10月. 1979(12. 10. 79)、特許請求の範囲(ファミリーなし)	1-6
A	US 3865903 A(Mobil Oil Corpotation), 11. 2月. 1975(11. 02. 75), 特許請求の範囲(ファミリーなし)	1-6
A	US 3937762 A(Mobil Oil Corpotation), 10. 2月. 1976(10. 02. 76), 特許請求の範囲&DE 2428462 A1	1-6